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Phase III: Laboratory Investigation of Portable Instruments for Submarine Air Monitoring

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14. ABSTRACT

Dräger tubes are currently used to supplement the atmosphere analysis measurements made aboard U.S. Navy submarines. The submarine fleet has requested that these tubes be replaced with a less labor intensive measurement system. Due to recent developments in gas sensing instrumentation, it is possible to replace many of the existing detectors with instruments that will incorporate more than one sensor at a time. This report is a continuation of an evaluation of portable instruments for use in submarines as air monitors. This is the third phase of a three-phase program concerned with investigating potential detection methods to replace the Dräger tubes. Phase III evaluated sensors for nitrogen dioxide, ammonia, sulfur dioxide, chlorine, hydrogen, and ozone. The chlorine and ozone sensors did not have sufficient sensitivity to detect the Navy 90-day limits. All of the manufacturers have ammonia sensors that can detect the 90-day limit. The Dräger ammonia was the best overall. The Omni nitrogen dioxide sensor was best overall for that test gas. The hydrogen sensors performed well. The sulfur dioxide sensor is not satisfactory.

15. SUBJECT TERMS

Submarine air monitoring; Portable air monitors; Vapor detectors; Electrochemical sensors; Nitrogen dioxide; Ammonia; Sulfur dioxide; Chlorine; Hydrogen; Ozone

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PHASE III: LABORATORY INVESTIGATION OF PORTABLE INSTRUMENTS FOR SUBMARINE AIR MONITORING

1.0 BACKGROUND

The submarine atmosphere is a unique controlled and monitored environment in which sailors live and work for extended periods of time. Atmosphere monitoring is principally done with the Central Atmosphere Monitoring System (CAMS), which is used to monitor life gases, permanent gases and some trace constituents. However, seventeen different detectors, primarily colorimetric (Dräger) tubes, are currently used to supplement the atmosphere analysis measurements made aboard US Navy submarines. As summarized in Table 1, there are a variety of circumstances under which these measurements must be made. In many cases, weekly measurements are required to supplement information obtained from CAMS. However, critical measurements are also made after casualty situations, such as a fire, or in drills for casualty situations. For example, carbon dioxide (CO_2), carbon monoxide (CO), hydrogen cyanide (HCN), and hydrogen chloride (HCl) levels must be monitored in a compartment for two hours after a fire. In gas free engineering applications, spaces are checked for CO, CO_2, oxygen (O_2), and combustible gas levels prior to entry into a space. Table 1 summarizes the Dräger tubes that are required, the situations under which they must be used, and the measurement level at which they must be employed. This requires that a supply of tubes, costing $4000 per year per submarine, be placed on board. Detector tubes have a limited shelf life, usually 2 years, and may expire before use. Most importantly, Dräger tube measurements give relatively slow response, are tedious, and require careful handling to be truly accurate. Even if used completely as specified, there is a degree of subjectivity in reading the colorimetric reactions on the tube. Consequently, there is little faith placed in the results and drills with the tubes are seldom properly conducted. The submarine fleet has requested that these tubes be replaced with a more modern, less labor intensive measurement system. Given the state of development of gas sensing instrumentation, it is possible to replace many of the existing Dräger tubes with instruments that will incorporate more than one sensor at a time. While it is unlikely that all of the existing tubes can be replaced with sensor packages in a cost effective manner, a good portion of the tubes outlined in Table 1 can be replaced.

It should be noted, however, that the submarine atmosphere is a unique environment. Simple deployment of off-the-shelf technology as direct drop-in replacements, while possible in some cases, is not advisable. For example, deployment of electrochemical sensors for CO detection will not work unless cross sensitivity for hydrogen is eliminated or compensated. Hydrogen levels aboard the submarine can vary extensively but are allowed to rise as high as 10,000 ppm. Consequently, any CO sensor with cross reactivity for hydrogen will generate false alarms when operations such as battery charging are carried out. Other considerations of note are the absence of significant amounts of onboard storage for calibration standards and bulky equipment. Therefore sensors chosen for these applications must have long shelf lives and low drift so that constant recalibration, onboard or shore side, is not required. Finally, the replacement measuring devices must require a minimal amount of intervention by ship's force.

Manuscript approved August 20, 2004.

Table 1. Compounds Evaluated with Dräger Tubes in Submarines

Compound	90-Day limit (ppm)	24-hour limit (ppm)	1-hour emer-gency limit (ppm)	Measure-ment range (ppm)	Weekly	Damage Control	Escape and Rescue	Gas-free Engin-eering
Acetone	200	1000	6000	20-9000	X			
Ammonia	10	100	100	0-150	X		X	
Benzene	0.1	2	50	0.1-75	X			
Carbon Dioxide	0.5%	4%	4%	0.05%-6%	CAMS X	X	X	X
Carbon Monoxide	20	50	400	2-600	CAMS X	X	X	X
Chlorine	0.1	0.5	3.0	0.05-4.5	X		X	
Combustible Gas				10% LEL to 25% LEL				X
Hydrocarbons	60 mg/m^3			6-600 mg/m3	X	X		
Hydrochloric Acid	0.5	20	20	0.05-30	X	X	X	
Hydrogen Cyanide	1.0	4.0	4.5	0.5 - 50		X	X	
Hydrogen Sulfide	1.0	3.0		2-500	X	X	X	
Monoethanolamine Ammonia	0.5	3	50	0.05-75	X			
Nitrogen Dioxide	0.5	1	1	0.05-1.5	X		X	
Oxygen	130-160 torr	130-160 torr	130-220 torr	100-250 torr	CAMS X	X	X	X
Ozone	0.02	0.1	1.0	0.005-1.5	X			
Sulfur Dioxide	1	5	10	0.1-15	X		X	
Toluene	20	100	200	2-300	X			
1,1,1-trichloroethane	2.5	10	25	0.25-37.5	X			

The technical objective of this effort was to procure, and test, in the laboratory and aboard ship, cost-effective replacements for the Dräger colorimetric tubes used for gas measurements aboard Navy submarines. In this effort, NSWC-CD/Philadelphia and Naval Research Laboratory (NRL), in consultation with NAVSEA, established a priority list of Dräger tubes to be replaced with appropriate handheld, portable sensors, with the goal of selecting replacement sensors that will cover as many applications (e.g. weekly atmosphere analysis, casualty etc) as is practicable. Once priorities were established, candidate sensor packages were selected. The sensor packages were selected to a) address measurement priorities and appropriate measurement ranges with sufficient accuracy, precision, and long-term reliability; b) maximize the number of sensors in a given instrument to minimize the number of instruments

that need to be procured; c) minimize the size and cost of the selected instruments; d) minimize the amount of calibration and replacement parts required. The test program was divided into three sections. Phase I tested instruments that can measure O_2, CO, hydrogen sulfide (H_2S), and combustibles (%LEL) [1]. Phase II evaluated sensors for CO_2, hydrogen cyanide (HCN), and hydrogen chloride (HCl), and broad range hydrocarbons (BRH) [2]. Phase III evaluates sensors for nitrogen dioxide (NO_2), ammonia (NH_3), sulfur dioxide (SO_2), chlorine (Cl_2), and ozone (O_3). This report describes Phase III laboratory test results. NRL was responsible for testing the sensors in the laboratory, assessing sensitivity, precision, accuracy and long-term drift of the instruments, as well as testing for cross sensitivity based on our knowledge of the submarine atmosphere.

2.0 INTRODUCTION

Identification, selection and procurement of equipment for testing was based on the needs described in Table 1 and the priorities identified above. Candidate instruments were selected for testing using the following initial selection criteria:

a. **Measurement range**: From 10% of the 90-day limit to 50% above the 1 hour limit
b. **Environmental:** Temperature range: 20-50 °C, relative humidity 35-95%
c. **Interferences**: Cross sensitivities between sensors will be investigated. Hydrogen inference, particularly on the CO sensor is critical in these studies.
d. **Accuracy**: Short-term accuracy; ± 10% relative over the specified measurement range, within 10 minutes of calibration. Long-term accuracy; ± 25% relative over the specified measurement range for up to 1 year after calibration
e. **Reproducibility**: ± 10% for measurements made within 10 minutes, over entire measurement range.
f. **Size**: Less than 0.5 cubic foot volume.
g. **General features**: Rugged, reliable, user friendly and field compatible, with capability to integrate several sensors into the same platform
h. **Cost:** Integrated procurement and maintenance calibration costs over the instrument lifetime not to exceed the cost of equivalent number of Dräger tubes over the same period

Four different manufacturers' instruments were utilized in Phase III testing. These are the Dräger Multiwarn II (Dräger), Enmet Omni 4000 (Omni), Industrial Scientific iTX (iTX), and the Biosystems PhD5 (PhD5). The sensors for Phase III testing were nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ammonia (NH_3), chlorine (Cl_2), and ozone (O_3). Sensors for four of the five Phase III gases were tested in all four of the manufacturers' instruments. The Enmet Omni is the only manufacturer that provides an O_3 sensor. For much of the Phase III testing, two each of the four prescribed instruments were used, for a total of eight instruments. For each manufacturer, one instrument contained an NH_3 and a Cl_2 sensor and the second unit contained a NO_2 and a SO_2 sensor. The Omni containing NO_2 and SO_2 sensors was also equipped with an O_3 sensor. In addition, the Dräger and Omni instruments containing NH_3 and Cl_2 sensors were also equipped with hydrogen (H_2) sensors. Dräger and Omni H_2 sensors were included in Phase III tests primarily to monitor their long-term performance. Coincidentally the H_2 sensors were tested for interference with some of the Phase III gases. The short-term performance of hydrogen

sensors was observed in Phase I. It was determined then that H_2 sensors are necessary when using carbon monoxide (CO) sensors due to the high cross sensitivity of CO sensors for H_2. Since a H_2 sensor will be included when CO sensors are used, their long-term performance was evaluated during Phase III.

Phase III was designed to evaluate the precision and accuracy of the sensors. Laboratory testing included short-term testing, interference testing, and long-term testing. Short-term testing included exposures to single components repeated over several days prior to the long-term sensor evaluation. Interference testing included each of the test gases in this phase of testing as well as hydrogen. The effect of relative humidity was evaluated by varying the relative humidity during regular long-term exposures of some test gases. The numerous cross interferences of the sensors in this phase of testing demanded that regular long-term testing use single analyte exposures of each Phase III gas rather than using a mixture of test gases as done in earlier phases.

3.0 EXPERIMENTAL

A vapor generation system was configured using mass flow controllers and a mixing chamber to generate a known concentration in clean air at a given relative humidity (RH). Zero-grade air was generated by passing house-compressed air through a series of demisters to remove any oil vapors, a reciprocating dual-tower molecular sieve scrubber, a hydrocarbon trap, and finally through a Purafil canister. The air was humidified to the desired level either by passing it through distilled deionized water or a Miller-Nelson (MN) Flow Control System, that controls the temperature and humidity of the purified air. For most tests, the air was kept at approximately 25°C with 50% relative humidity. Calibrated gas cylinders are used to generate the test vapors at a given concentration. Matheson, Tylan, and Sierra Mass Flow Controllers were used to control the flow of the test gases. These gases are mixed with clean air to create a specific concentration of analyte. Each test instrument sampled the same air off the sample manifold. Figure 1 shows a diagram of the test manifold used.

The instruments were exposed to clean, humidified air for 15 minutes, then the test vapor for 15 minutes, and finally to the clean air for 15 minutes. They were not exposed to another test vapor until they had fully cleared down. Instruments were re-zeroed as needed in clean air. Short-term testing was completed as soon after the sensors were installed as possible. The instruments were exposed to test vapors across the measurement range. The effects of relative humidity were determined by exposing the instruments to a range of test vapor concentrations in low, medium, and high levels of relative humidity. The instruments were evaluated for cross sensitivities by exposing them to single component air steams. The hydrogen cross sensitivity was thoroughly evaluated. Long-term tests were conducted over several weeks, and consisted of frequent application of single component air streams to the instruments.

4.0 RESULTS

4.1 Short -Term Testing

Short-term testing consists of multiple exposures of single components. These tests are performed to specifically assess a sensors' factory calibration and to initially determine any cross sensitivities among sensors. The data collected in this time period serves as a quantitative measure of the performance of a sensors' factory calibration. Figures 2, 3, 4, 5, and 6 depict Omni short-term sensor performance. Plots of this type represent sensor responses versus applied concentration. The equations for each plot shown are representative of the response of each sensor. A slope of 1, an intercept of 0, and a R^2=1 are representative of an ideal response. Short-term performance plots for every sensor and instrument tested appear in Appendix A.

Meeting the detection requirement at ten percent of the Navy 90-day limit is a challenge for all the sensors in this phase. The ammonia sensors all provided a good response at 10 ppm, and all but the iTX were able to detect as low as 5 ppm. The nitrogen dioxide and sulfur dioxide sensors are able to detect 90-day limits, but the responses are at the lower detection limit. The chlorine and ozone sensors do not meet the 90-day limits. Having reviewed the factory calibration, short-term performance of all four instruments' sensors on the basis of slope, intercept, and R^2 the sensors are ranked from better to worse in this category. The results of this evaluation are displayed in Table 2. Note that the sensors are organized by sensor type and they are listed within each type from left to right in order of best to worst performance.

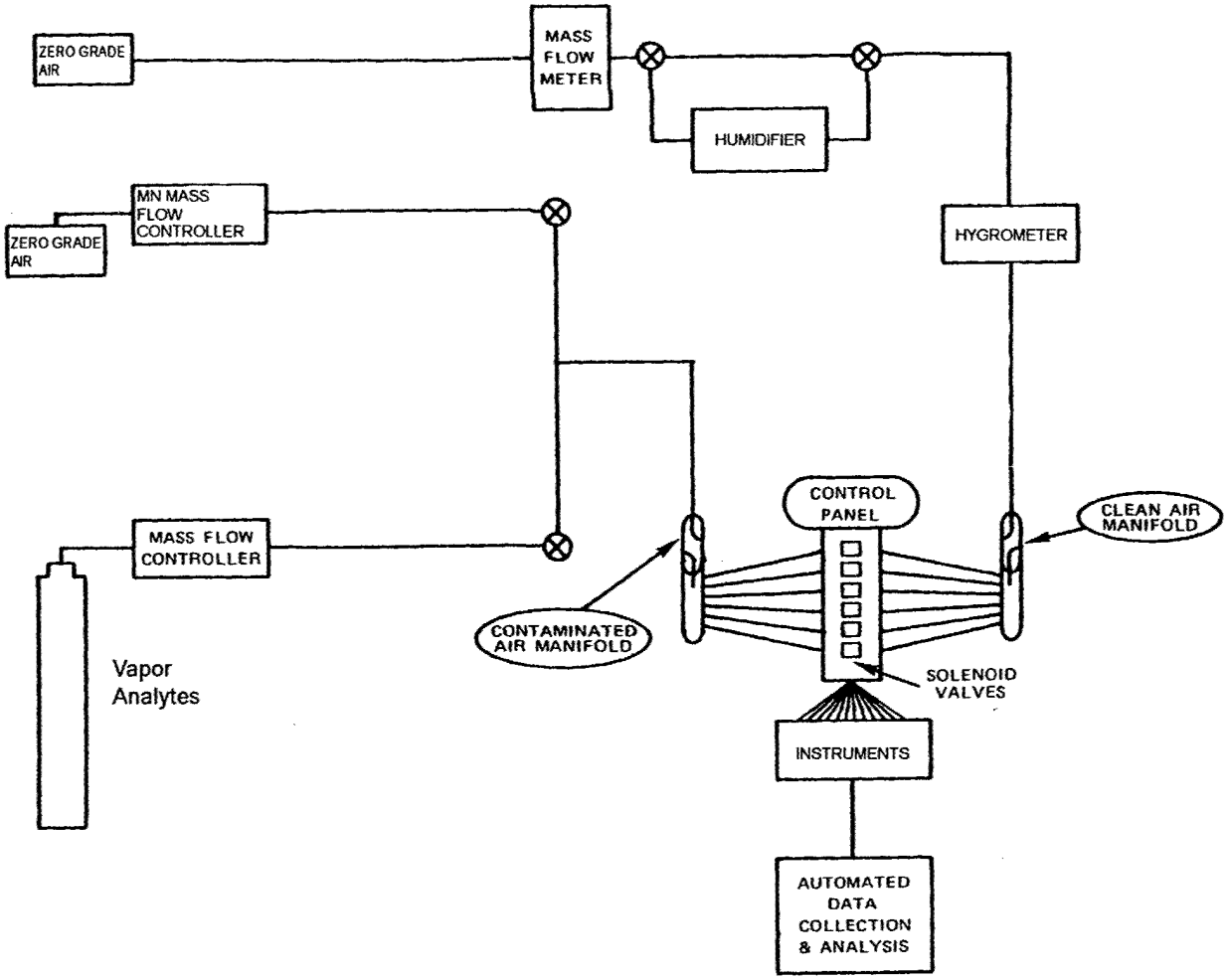


Figure 1. Test manifold designed for the instrument evaluation.

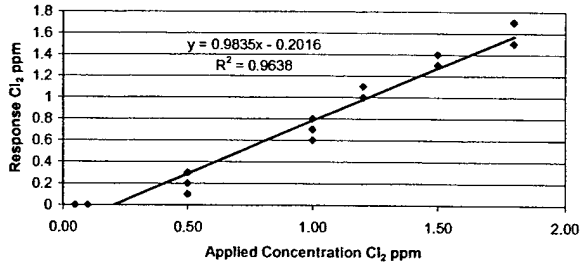


Figure 2. Omni Cl_2 Sensor

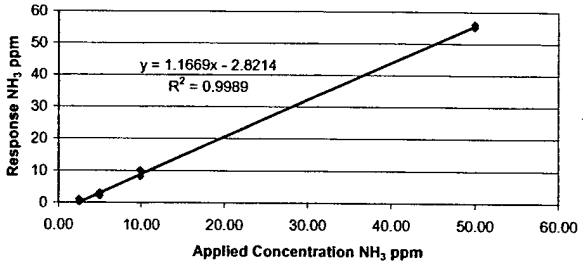


Figure 3. Omni NH_3 Sensor

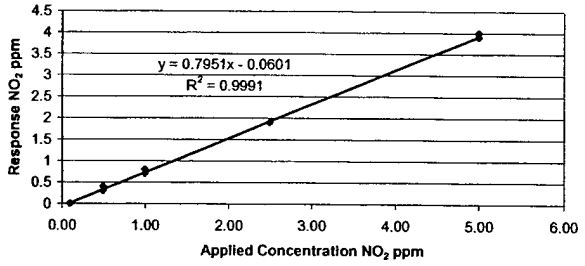


Figure 4. Omni NO_2 Sensor

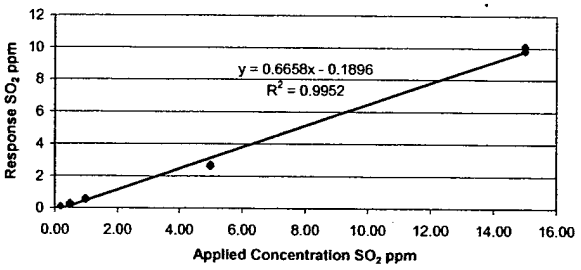


Figure 5. Omni SO_2 Sensor

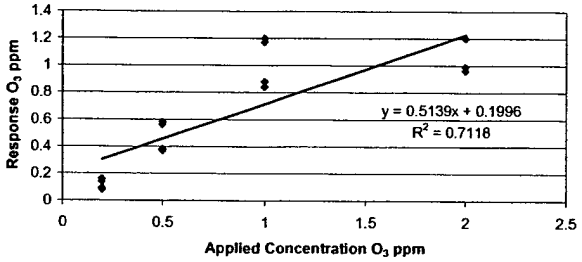


Figure 6. Omni O_3 Sensor

Table 2. Short Term Performance Summary

	Cl_2				NH_3				NO_2				SO_2				O_3
Sensor	Omni Cl_2	iTX Cl_2	Drager Cl_2	PhD5 Cl_2	Drager NH_3	Omni NH_3	PhD5 NH_3	iTX NH_3	iTX NO_2	Drager NO_2	Omni NO_2	PhD5 NO_2	Drager SO_2	iTX SO_2	Omni SO_2	PhD5 SO_2	Omni O_3
Slope	1.0	0.6	0.3	0.1	1.1	1.2	0.7	1.2	0.9	0.9	0.8	0.7	0.8	1.2	0.7	0.7	0.5
Intercept	-0.20	-0.37	-0.10	-0.07	-1.61	-2.82	-0.87	-4.79	0.13	-0.09	-0.06	-0.04	-0.43	-0.65	-0.19	-0.37	0.20
R^2	0.96	0.85	0.91	0.84	1.00	1.00	0.99	1.00	1.00	1.00	1.00	1.00	0.98	0.99	1.00	0.96	0.71

4.2 Observed Phase III Cross Sensitivities

The cross sensitivities among the sensors used for Phase III gases are large. Some of these responses make the sensors unsatisfactory for some applications. In the submarine environment, any hydrogen cross sensitivities will impact the usefulness of the sensor because the hydrogen concentration varies and is allowed to rise as high as 10,000 ppm. All of the observed Phase III interferences are summarized in Table 3. Highlighted cells in this table indicate the most substantial cross sensitivities. Where appropriate, plots for these highlighted cross sensitivities are found in Appendix B.

Table 3. Phase III Cross Sensitivities

Exposure Gas →		SO_2	NO_2	Cl_2	NH_3	O_3	H_2
Test Interval →		0.2 - 15 ppm	0.1 - 5 ppm	0.05 - 5 ppm	2.5 - 100 ppm	0.01 - 1 ppm	30 - 950 ppm
	Sensor ↓						
Dräger	NH_3	X	X	X	-		X
	Cl_2	INV @clear down after 15 ppm	Trend, 0.1 @5 ppm	-	X		X
	H_2			X	X		-
	NO_2	INV @≥5 ppm	-	Trend, 0.5 @ 5 ppm	X		X
	SO_2	-	INV @≥2.5 ppm	X	X		Trend, 0.7 @925 ppm
Omni	NH_3	X	Trend, 1 @5 ppm	X	-		Trend, –13 @125 ppm, Faults @≥330 ppm
	Cl_2	0.1 @≥5 ppm	Trend, 6 @5 ppm	-	0.1 @≥5 ppm		X
	H_2			X	X		-
	NO_2	X	-	Trend, 0.25 @5 ppm	X	0.2 @1 ppm	X
	SO_2	-	Trend, 3 @5 ppm	Trend, 0.9 @5 ppm	X	0.2 @1 ppm	X
	O_3	Trend, -0.1 @3 ppm, Faults @≥5 ppm	Trend, 0.6 @3 ppm	Trend, 1.2 @2.5 ppm, Faults @5 ppm	Faults @≥5 ppm	-	Trend, 0.07 @925 ppm
PhD5	NH_3			X	-		X
	Cl_2			-	X		X
	NO_2	X	-				X
	SO_2	-	Trend, -2.5 @5 ppm				Trend, 0.4 @925ppm
ITX	NH_3	Trend, 1.5 @5 ppm	X	X	-		Trend, –35 @925 ppm
	Cl_2	1.7 @15 ppm	Trend, 2.5 @5 ppm	-	X		X
	NO_2	X	-	Trend, 1 @5 ppm	X		X
	SO_2	-	Trend, –6 @5 ppm	-0.6 @5 ppm	X		0.4 @925 ppm

X = No sensor response was observed in the specified range.

\- = Responses for matching sensor types and exposures are withheld from this table.

"blank" = Exposure gas was not applied to the corresponding sensor.

Trend = Sensor showed a response trend over all or some part of the specified range. Sensor responses for interferences are reported (in ppm) at a designated exposure concentration or condition i.e. 0.1 @5 ppm.

INV = Invalid response specific to the Dräger instrument

4.3 Hydrogen Sensor Testing

As seen in Figures 7 and 8, the Dräger and Omni H_2 sensors were tested at four different concentration levels on three separate occasions over the course of a two-week period. The Dräger's H_2 response was elevated when compared with the delivered concentration. Over the two weeks of H_2 testing, the Dräger showed about a 3% drop in response at the 33 ppm, 123 ppm, and 337 ppm testing levels. The Dräger also consistently showed its maximum response of 1000 ppm at the 900 ppm H_2 level. The Omni's response was less precise than that of the Dräger, but the accuracy of the response relative to the delivered H_2 concentration is better.

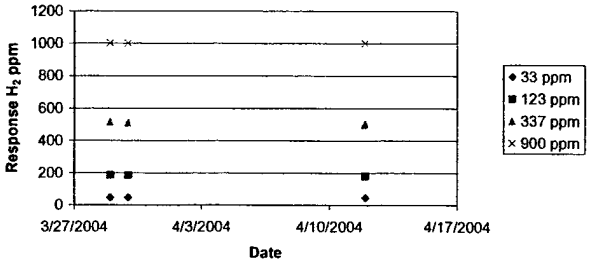


Figure 7. Dräger H_2 Sensor

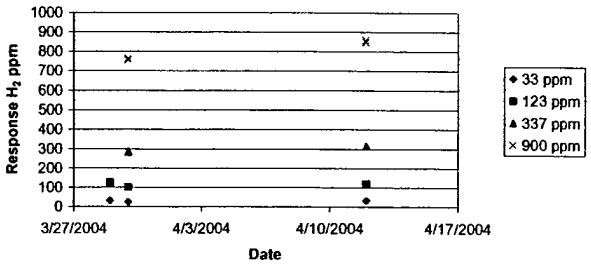


Figure 8. Omni H_2 Sensor

4.4 Humidity Testing

The instruments were tested at three different concentration levels for both NH_3 and NO_2 at 35%, 50 %, 85% RH. For ammonia, the effects of the humidity cannot be determined because the day to day variance in the responses is greater than the changes in response due to RH as shown in Figure 9. Data collected at 50 % RH is not displayed in Figure 9, because the results show the same trend and it would only serve to clutter the image.

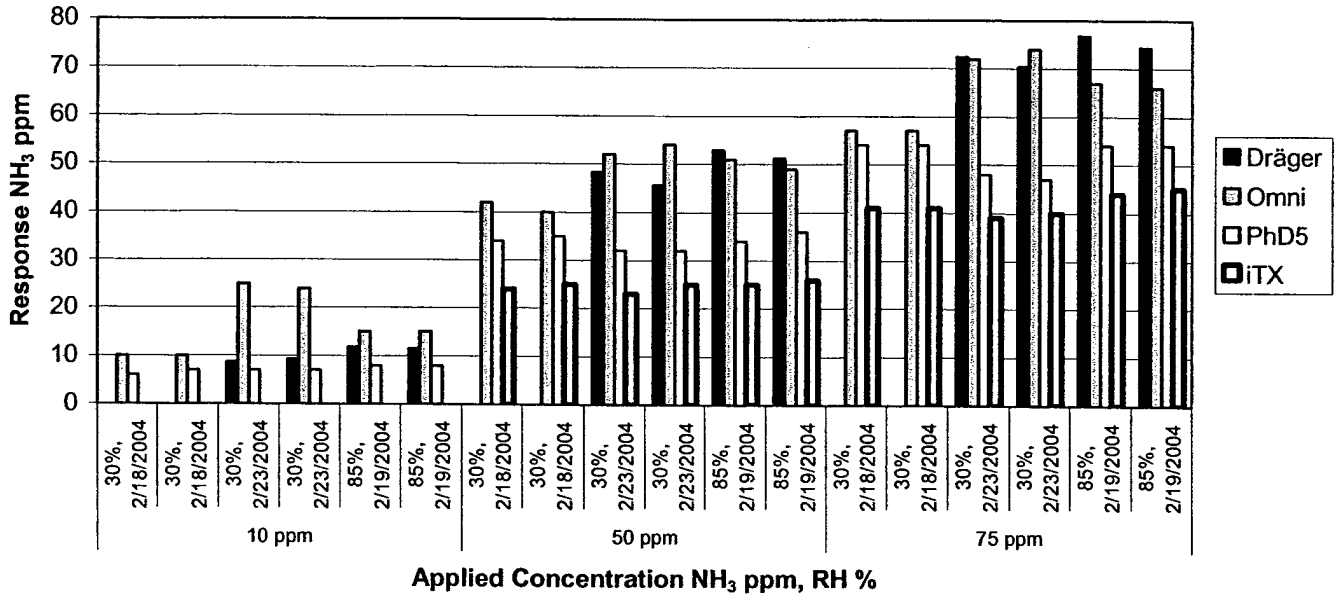


Figure 9. NH_3 Sensor Relative Humidity Interference Summary

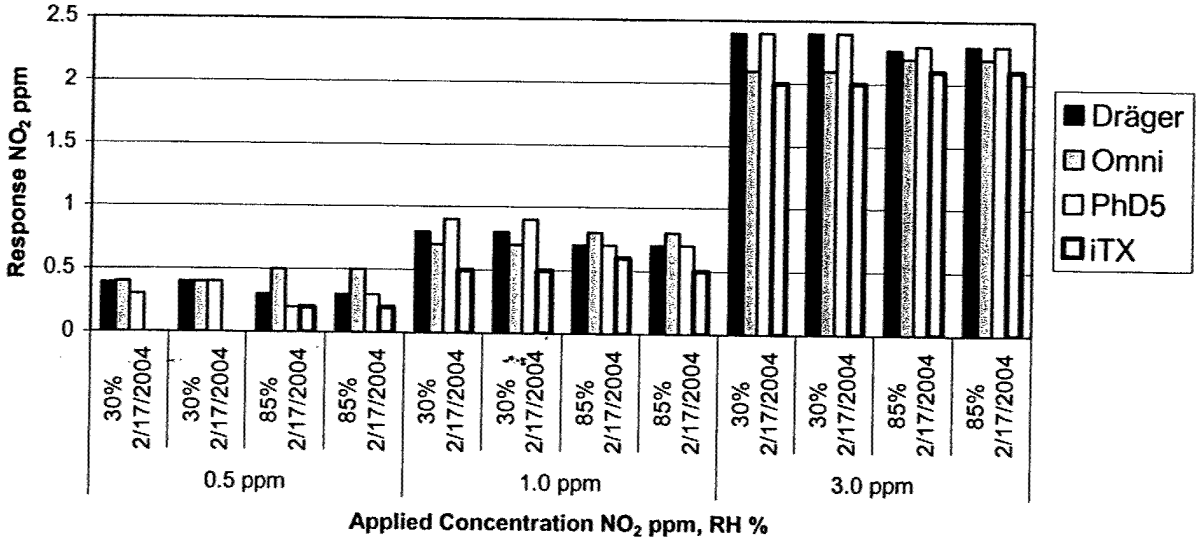


Figure 10. NO_2 Sensor Relative Humidity Interference Summary

The NO_2 humidity testing was performed over the course of one day. As seen in Figure 10, both the Dräger and PhD5 NO_2 sensor responses were slightly elevated at the 85% level of relative humidity. At the same time, the NO_2 responses of both the Omni and iTX NO_2 sensors were slightly decreased at the 85% level of relative humidity. All four instruments were tested simultaneously so the observed differences at the practical extremes of relative humidity tested (35% RH and 85% RH) are certainly indicative of the effect of relative humidity on these four instruments NO_2 sensors. The effect is not however great enough to warrant concern.

4.5 Omni Ozone Sensor Performance

The only O_3 sensor available for testing was the Omni with a detection range of 0.05 to 1.00 ppm at best. Even a brand new O_3 sensor would not meet the 90-day limit of 0.02 ppm. The testing for this sensor was limited, but sufficient to indicate its limitations. Two O_3 sensors were tested prior to field deployment in late May 2003. The initial short-term performance of these two O_3 sensors is displayed in Figure 11.

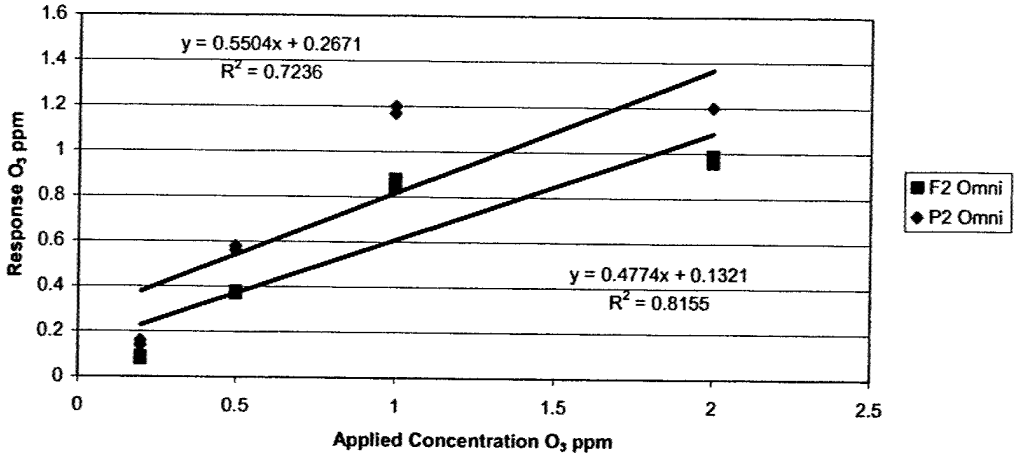


Figure 11. Short Term Data for Two New Omni O_3 Sensors

An additional Omni O_3 sensor was installed during the long-term testing of the Cl_2, NH_3, NO_2, and SO_2 sensors. Interference data for these gases with the O_3 sensor was acquired in addition to H_2 interference data. After exposure to the other test gases, this O_3 sensor was also exposed to several concentrations of O_3 and the responses are shown in Figure 12. The poor performance of the O_3 sensor for Navy applications is quite clear. The response below 0.2 ppm is zero. This is an order of magnitude above 90-day limit for O_3.

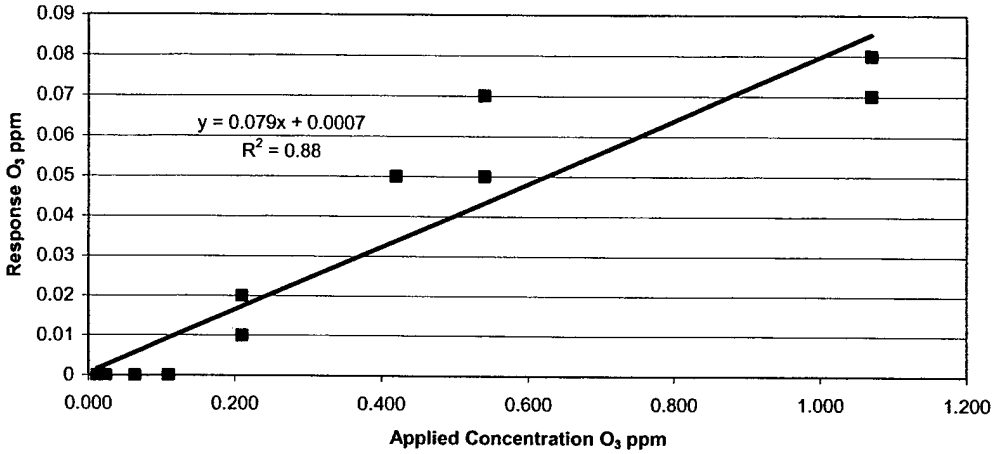


Figure 12. Post Long-Term CL_2, NH_3, NO_2, and SO_2 Testing, Omni O_3 Sensor Performance

The two field deployed O_3 sensors displayed a Fault condition following the Field Trial tests. Review of the Omni, O_3 row in Table 3 summarizes the various interferences the Omni O_3 sensor has with the other Phase III gases. The observed H_2 interference provides a likely explanation for the persistent Fault condition of the O_3 sensors returned from the field. Prolonged exposure to the submarine H_2 laden atmosphere likely poisoned the field tested O_3 sensors.

4.6 Long -Term Testing

The long-term performance of the four instruments' Cl_2, NH_3, NO_2, and SO_2 sensors was evaluated over a period of 8-10 weeks. The instruments were exposed to individual applications of each test gas on several occasions. Initial testing was performed by in late November and early December 2003. A final series of tests was performed throughout February 2004. There are some discrepancies between data collected in these two periods. Some data taken from the sensors during the initial period are not used in the analysis due to abnormally low responses. Most of the data from the initial testing period is acceptable and all data collected is displayed in Appendix C.

4.6.1 Long -Term Ammonia Sensor Performance

All four NH_3 sensors showed a decline in response over the test period, see Appendix C. This decline is most apparent in the iTX NH_3 sensor response over the entire 8-10 week period as shown in Figure 13. After the first month, the sensor does not detect 10 ppm, the 90-day limit for ammonia. The overall performance of the NH_3 sensors is displayed in Table 4.

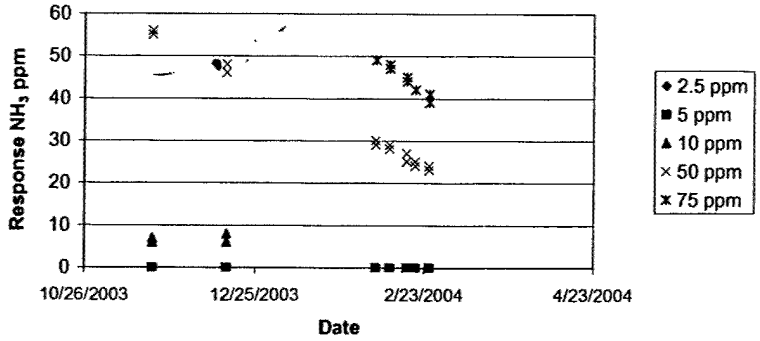


Figure 13. iTX NH_3 Sensor

The Omni (Figure 14) and Dräger (Figure 15) responses to ammonia are more stable than the iTX over the same test period. The Omni seems to improve after the application of the Omni's auto set (auto zeroing) procedure on 2/25/2004. The Omni NH_3 sensor however has a substantial negative cross sensitivity to H_2. Therefore the Dräger NH_3 sensor is the best choice for ammonia detection at the Navy 90-day limit.

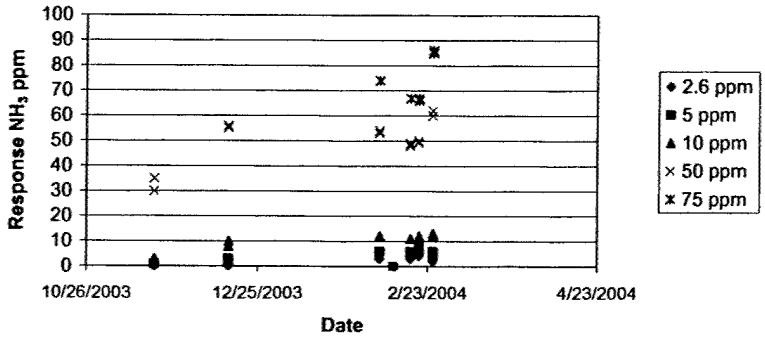


Figure 14. Omni NH_3 Sensor

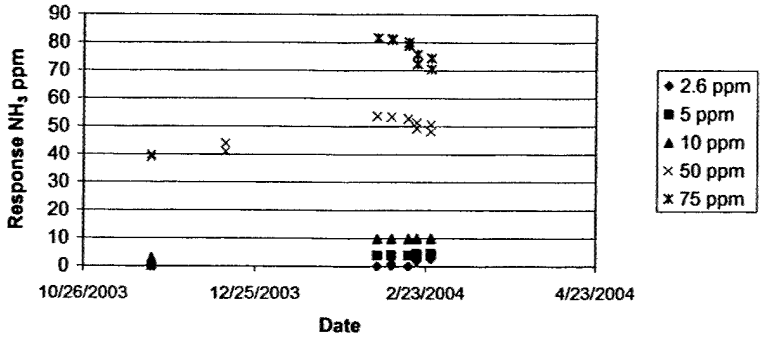


Figure 15. Dräger NH_3 Sensor

Table 4. NH_3 Long-Term Sensor Performance

NH_3	ppm	2.5	5	10	50	75
Dräger	Precision	+/- 55%	+/- 5%	<5%	<5%	<5%
	Accuracy	-45%	-15 %	-5%	+5%	+5%
Omni	Precision	+/- 40%	+/- 20%	+/- 10%	+/- 5%	+/- 5%
	Accuracy	+60%	+20%	+20%	<5%	-5%
iTX	Precision	No Response	No Response	No Response	At 50 ppm drop from 30 to	
	Accuracy	No Response	No Response	No Response	24 from 2004 Feb 6 to 25	
PhD5	Precision	+/- 40%	+/- 10%	+/- 5%	At 50 ppm drop from 38 to	
	Accuracy	-60%	-30%	-25%	30 from 2004 Feb 6 to 25	

4.6.2 Long -Term Chlorine Sensor Performance

During short-term testing, the Omni instrument performed better than the other instruments, but it still did not detect the 90-day limit of 0.1 ppm. In general, the performance of the Cl_2 sensors was poor, so long-term testing was limited. The Omni Cl_2 sensor demonstrates the best performance of the four instruments' Cl_2 sensors. The results were very inconsistent over the test period, as shown in Figure 16. The other sensor results are worse, see Appendix C. In addition, the Omni's Cl_2 sensor has substantial cross sensitivity to NO_2. Therefore, none of the chlorine sensors are recommended for use.

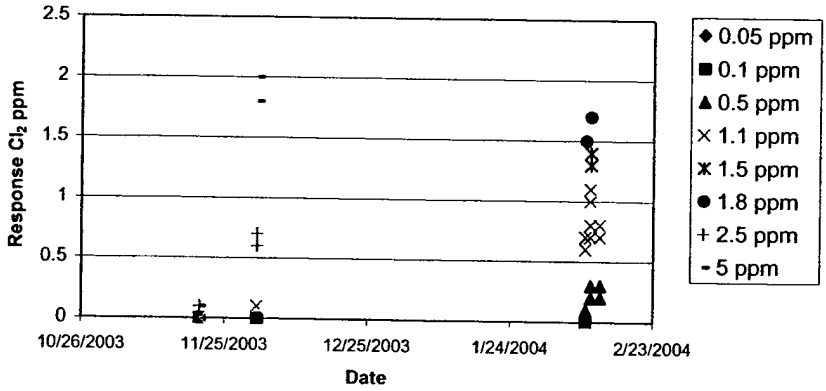


Figure 16. Omni Cl_2 Sensor

4.6.3 Long -Term Nitrogen Dioxide and Sulfur Dioxide Sensor Performance

The long-term performance of the NO_2 and SO_2 sensors is summarized in Tables 5 and 6. The Omni NO_2 sensor is the best of the four NO_2 sensors. It detects the 90-day limit and has adequate precision and accuracy to 0.1 ppm. The Omni NO_2 does have some minor cross sensitivities to Cl_2 and O_3 (see Table 3), but these are unlikely to cause a problem.

Table 5. NO_2 Long-Term Sensor Performance

NO_2	ppm	0.1	0.2	0.5	1	3
Omni	Precision	<5%	<5%	<5%	+/- 5%	+/-5%
	Accuracy	<5%	<5%	-20%	-15%	-25%
PhD5	Precision	No Response	+/-50%	<5%	+/- 5%	+/- 5%
	Accuracy	No Response	<5%	-20%	-15%	-25%
Dräger	Precision	No Response	No Response	<5%	<5%	<5%
	Accuracy	No Response	No Response	-20%	-20%	-20%
iTX	Precision	No Response	No Response	<5%	+/-5%	<5%
	Accuracy	No Response	No Response	-60%	-45%	-30%

At 1 ppm, the 90-day limit for sulfur dioxide, all of the sensors gave low responses, however the precision of the responses was good. The Omni sensor was the most precise and was able to detect the test gas below the 90-day limit. It does however have a substantial cross sensitivity to NO_2.

Table 6. SO_2 Long-Term Sensor Performance

SO_2	ppm	0.5	1	2	4	5
Omni	Precision	+/- 10%	+/- 5%	<5%	<5%	<5%
	Accuracy	-70%	-65 %	-65%	-65%	-60%
iTX	Precision	No Response	<5%	<5%	<5%	<5%
	Accuracy	No Response	-35%	-10%	<5%	+15%
PhD5	Precision	+/- 30%	+/- 30%	+/- 10%	+/- 10%	+/- 10%
	Accuracy	-70%	-70%	-50%	-40%	-35%
Dräger	Precision	No Response	+/- 10%	+/- 5%	<5%	<5%
	Accuracy	No Response	-60%	-50%	-45%	-40%

As seen in Figure 17, unlike any of the other NO_2 and SO_2 sensors tested the Dräger SO_2 showed a trend of increasing SO_2 response from 2/4/2004 to 2/26/2004. All other NO_2 and SO_2 sensors remained stable for the entire testing period.

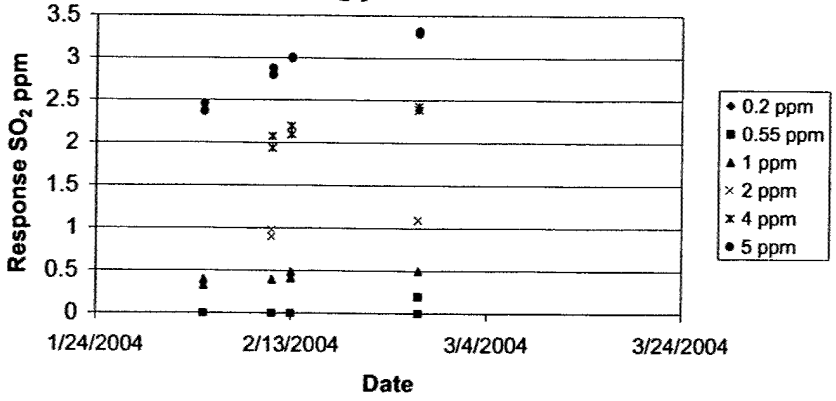


Figure 17. Dräger SO_2 Sensor

5.0 CONCLUSION

Sensors for Cl_2, O_3, NH_3, NO_2, SO_2, and H_2 were evaluated during Phase III. The chlorine and ozone sensors do not have sufficient sensitivity to detect the Navy 90-day limits. In addition, the Omni O_3 sensor, the only O_3 sensor available for testing, has little selectivity because it responded to all the test vapors. The Omni chlorine sensor had the best sensitivity, but the cross sensitivities with NO_2 and NH_3 made it unsatisfactory for most applications. The performance of the Dräger Cl_2 in this round of testing was very poor due to the extremely low responses relative to the delivered Cl_2 concentrations. The Dräger Cl_2 sensor also has cross sensitivities to NO_2 and SO_2.

For the other test gases, the results were better, but less than ideal. All the manufacturers have ammonia sensors that can detect the 90-day limit. The Dräger NH_3 was the best overall. The Omni and iTX NH_3 sensors have interferences with hydrogen. The Omni NO_2 sensor was the best overall for that test gas. The precision and accuracy was good down to 0.1 ppm. However, it did have cross sensitivities to chlorine and ozone. For sulfur dioxide, the precision was good for the Omni and iTX, but the accuracy was bad. The Omni consistently read 65% low, suggesting that the calibration was off. The iTX varied from 35% low at low concentrations to 15% high. In addition, the iTX and Dräger SO_2 sensors had cross sensitivities to H_2. The Omni SO_2 sensor is also cross sensitive to NO_2, chlorine, and ozone. The responses for the Dräger SO_2 varied over the 8-10 weeks of long-term testing, however it looked similar to the Omni in the short-term test and at the end of the long-term test.

The hydrogen sensors were included in this phase of testing because they are needed to compensate for the cross sensitivities that the Omni and Dräger CO sensors have for hydrogen. Both sensors looked good. The Dräger sensor was more precise than the Omni, but the Omni was more accurate. Neither sensor had cross sensitivities for chlorine or ammonia. However, in Phase I tests, it was determined that the Dräger H_2 sensor was sensitive to CO and the Omni was not [1].

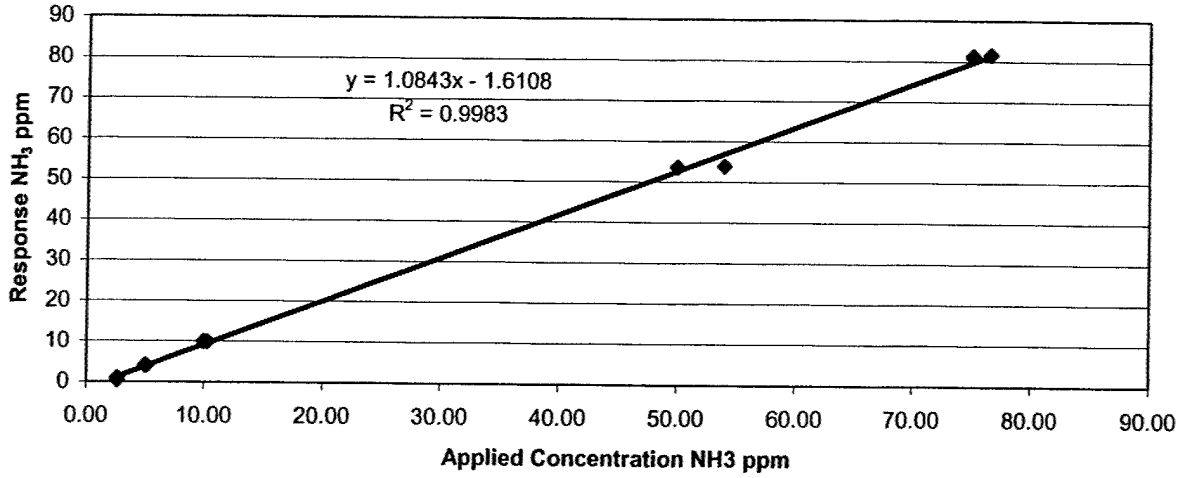
6.0 REFERENCES

1. Evans, T.W., Werner, J., Rose-Pehrsson, S.L., Hammond, M.H., and Callahan, J., "Phase 1: Laboratory Investigation of Portable Instruments for Submarine Air Monitoring," NRL/MR/6110—03-8704, 29 August 2003.

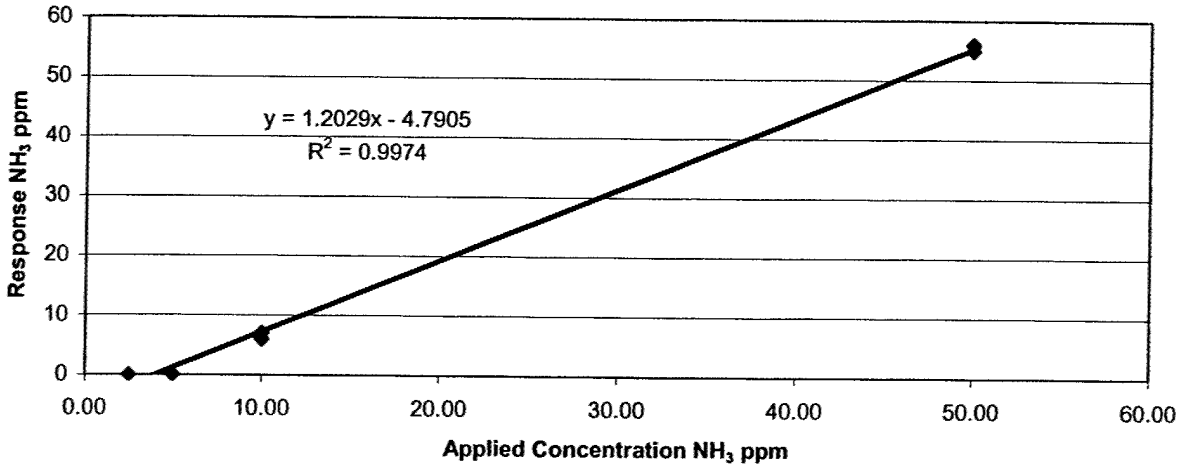
2. Werner, J.M., Evans, T.W., Rose-Pehrsson, S.L., and Hammond, M.H., "Phase II: Laboratory Investigation of Portable Instruments for Submarine Air Monitoring," NRL/MR/6110—03-8753, 27 February 2004.

Appendix A

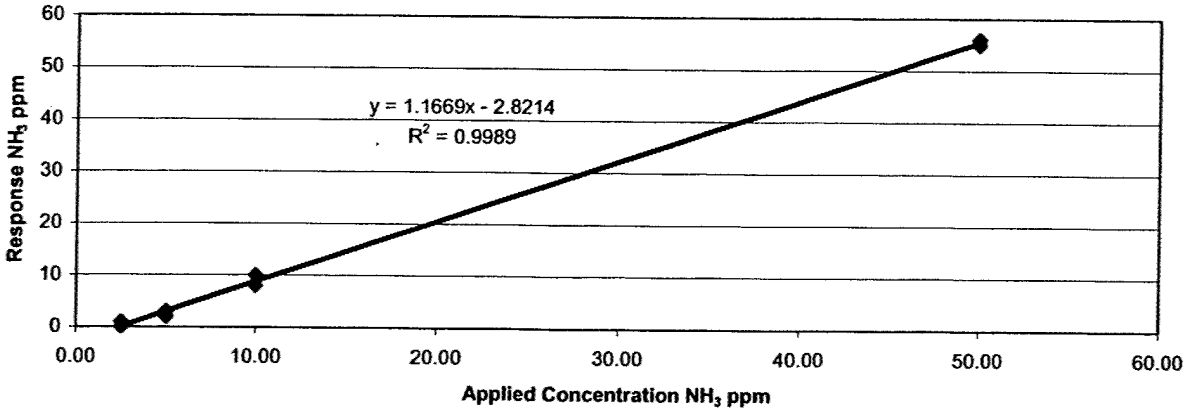
Dräger NH_3



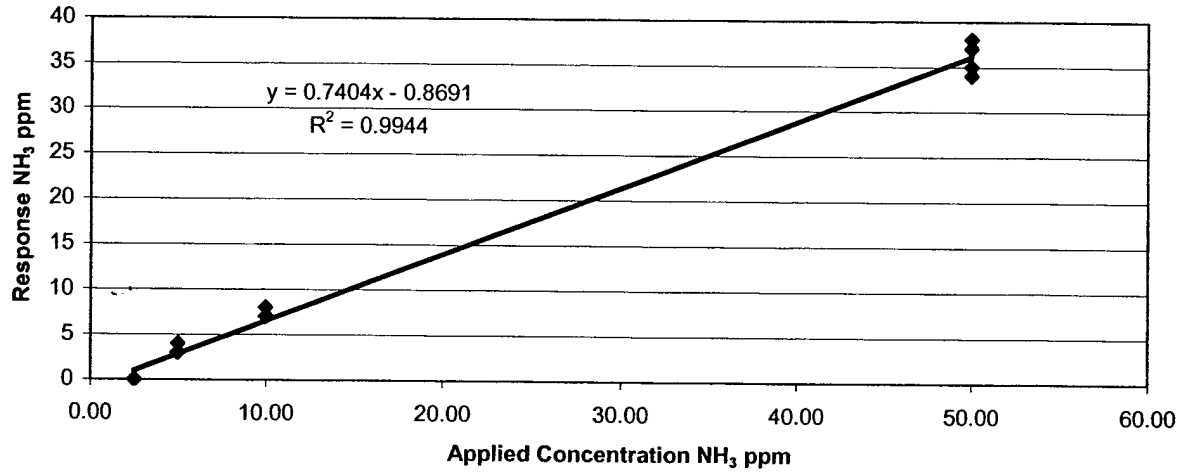
iTX NH_3



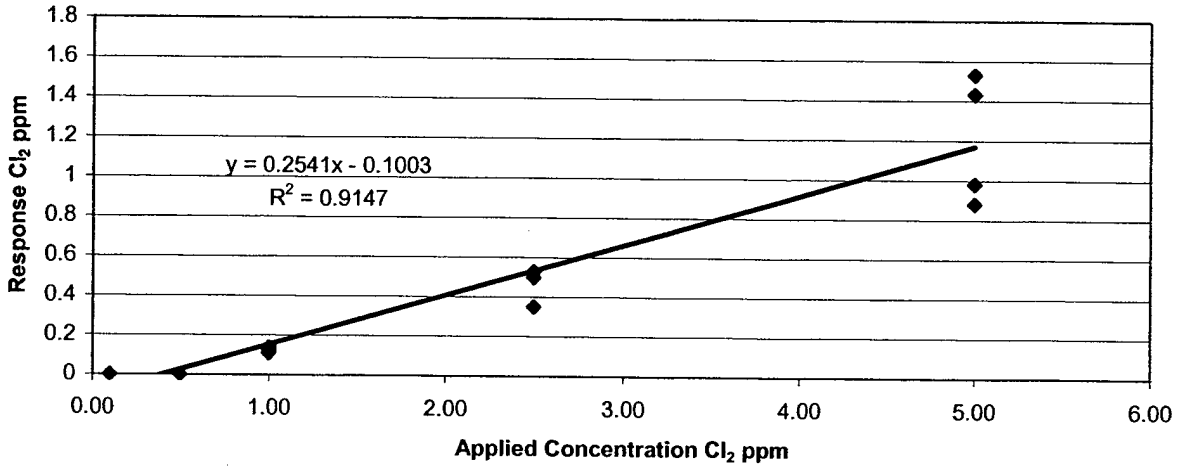
Omni NH_3



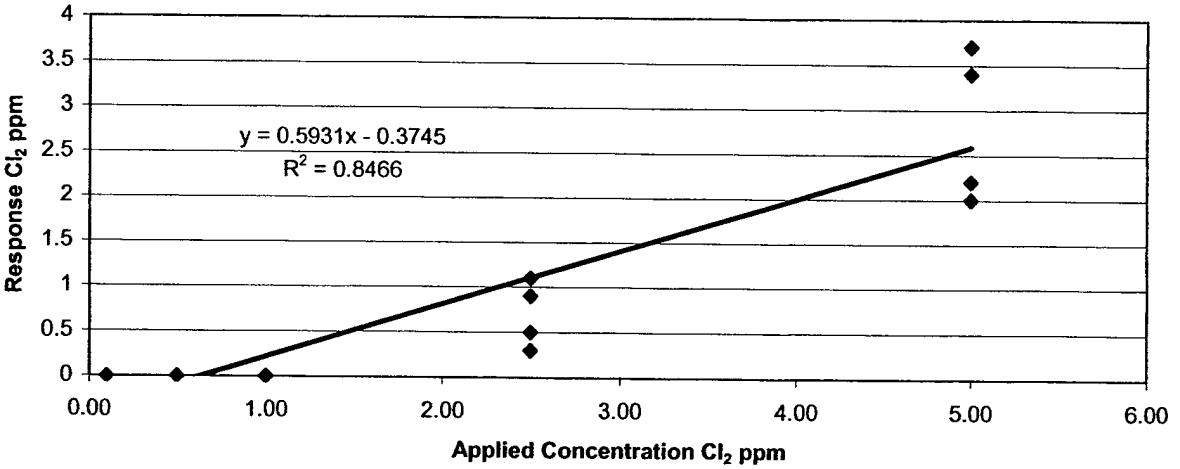
PhD5 NH_3



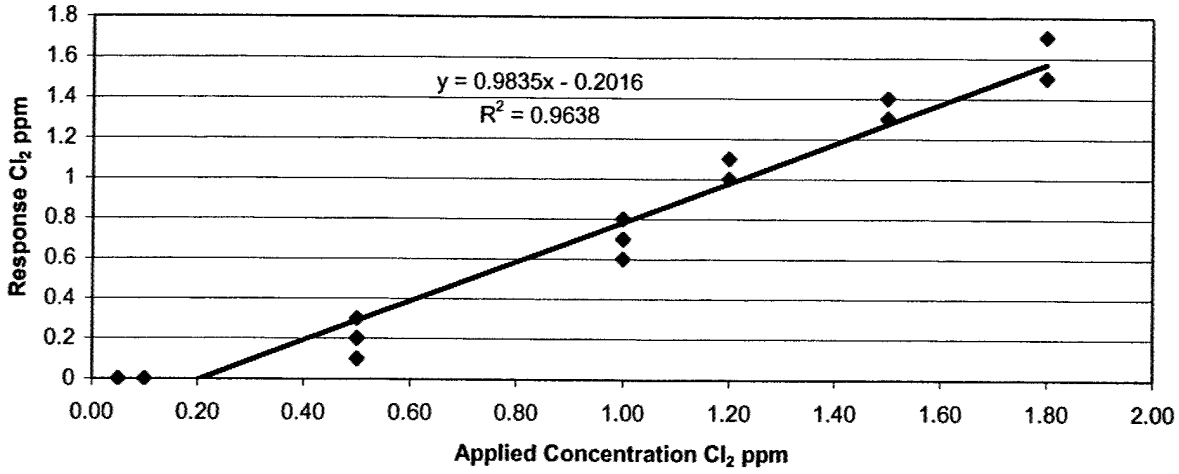
Dräger Cl_2



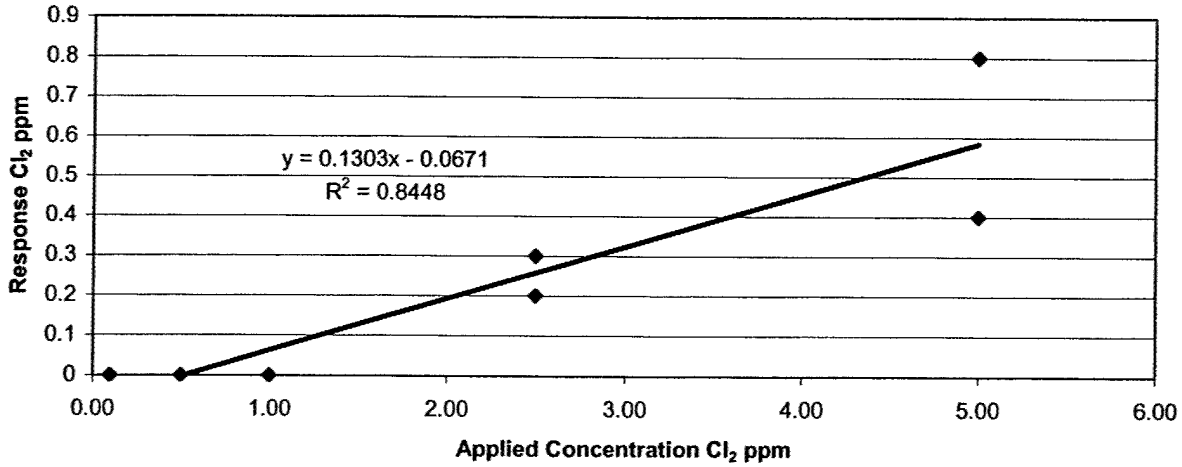
iTX Cl_2



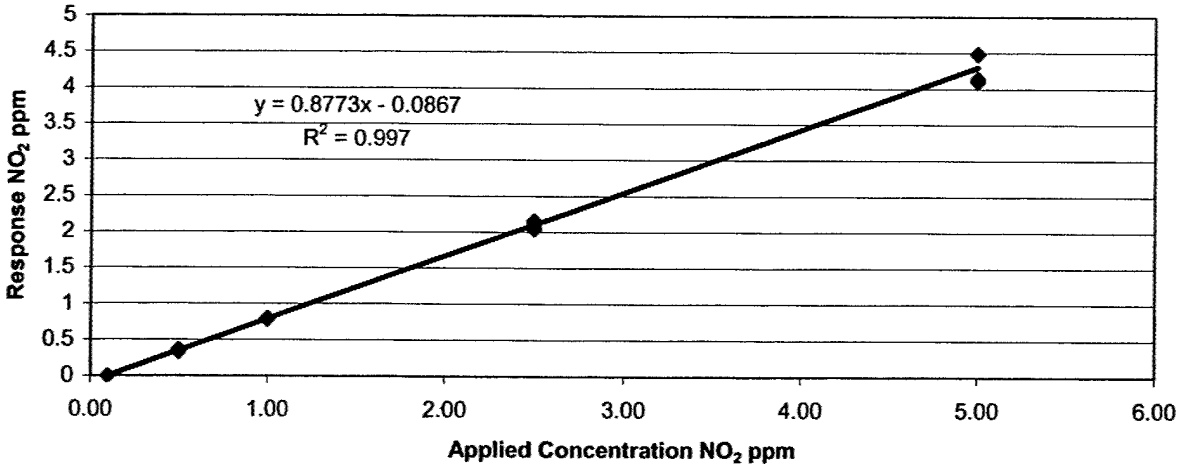
Omni Cl_2



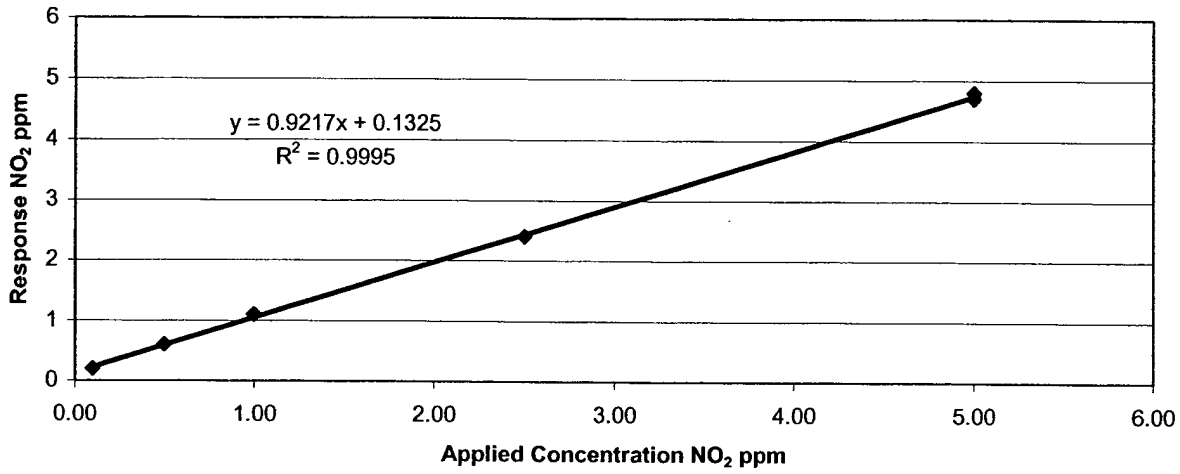
PhD5 Cl_2



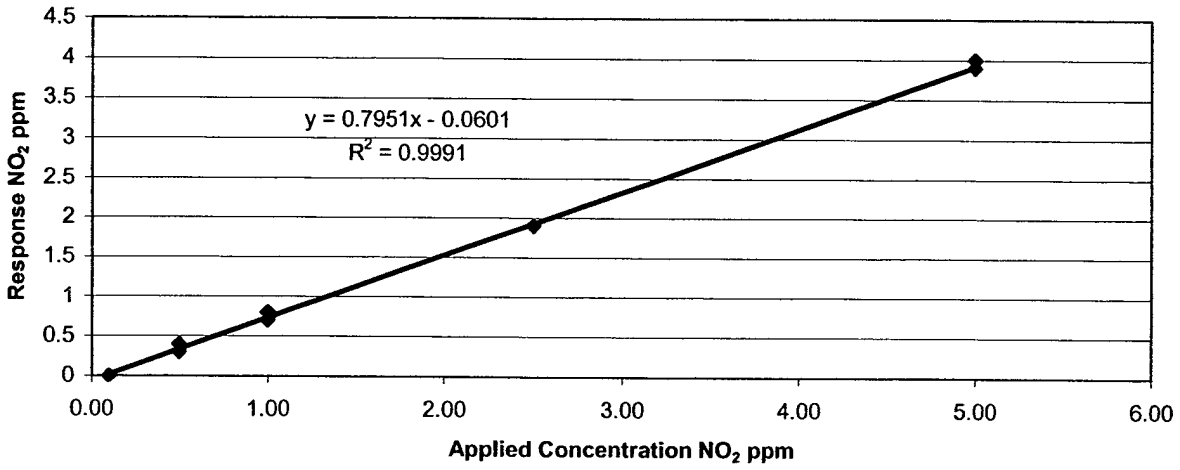
Dräger NO_2



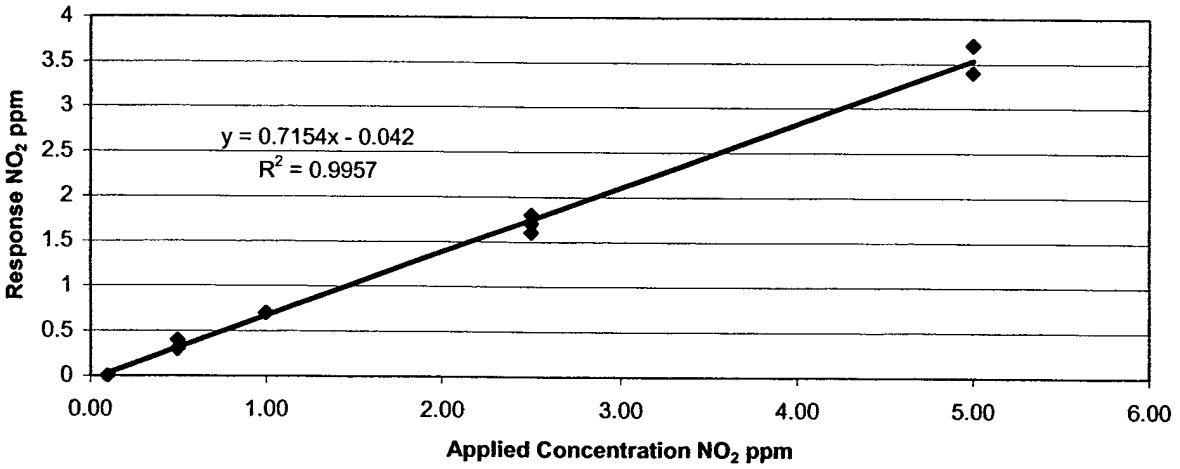
iTX NO_2



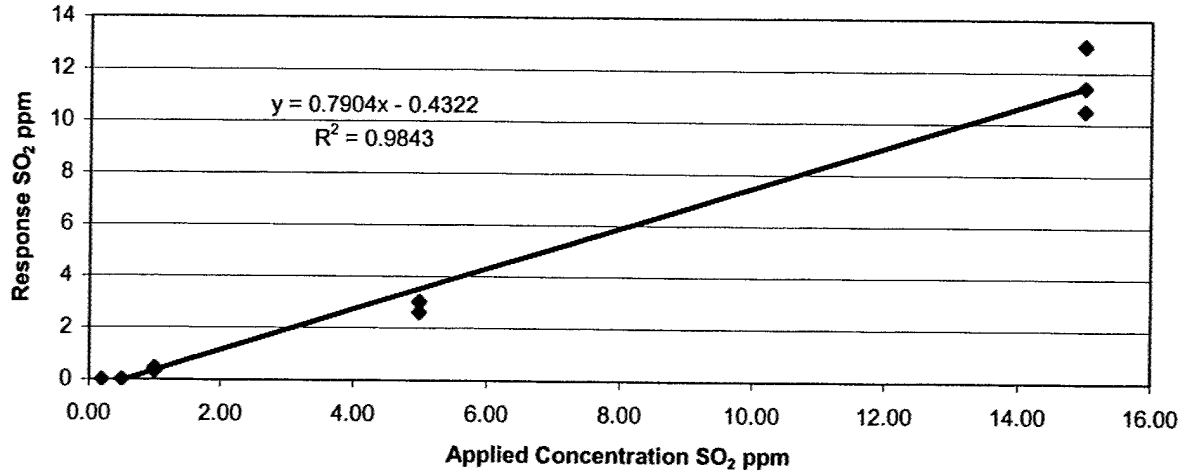
Omni NO_2



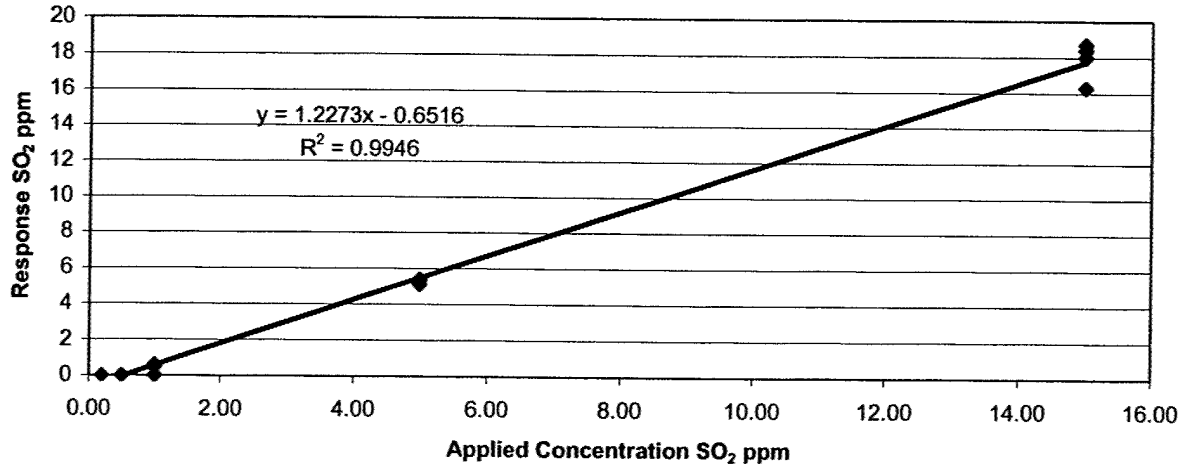
PhD5 NO_2



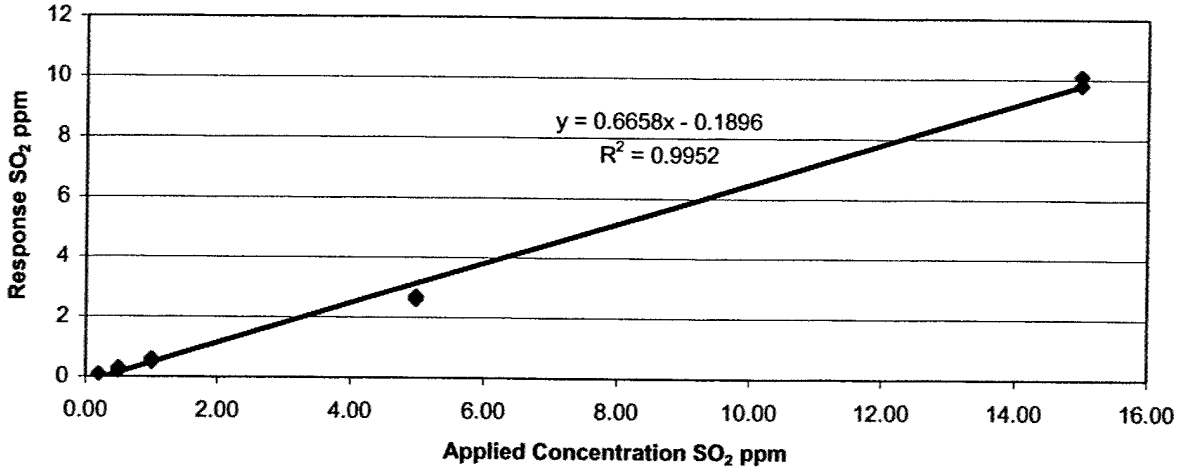
Dräger SO_2

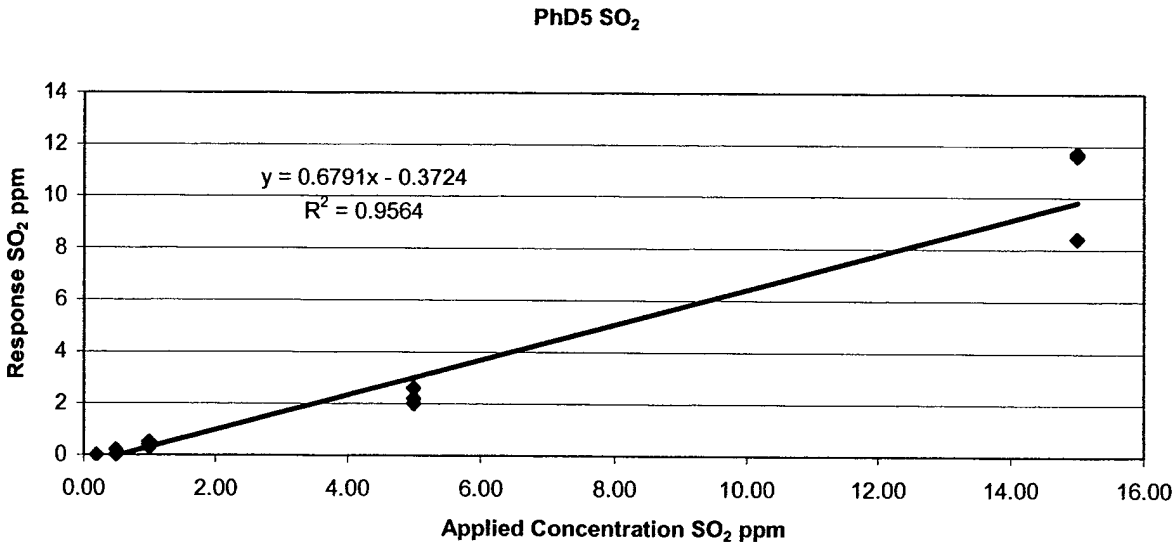


iTX SO_2

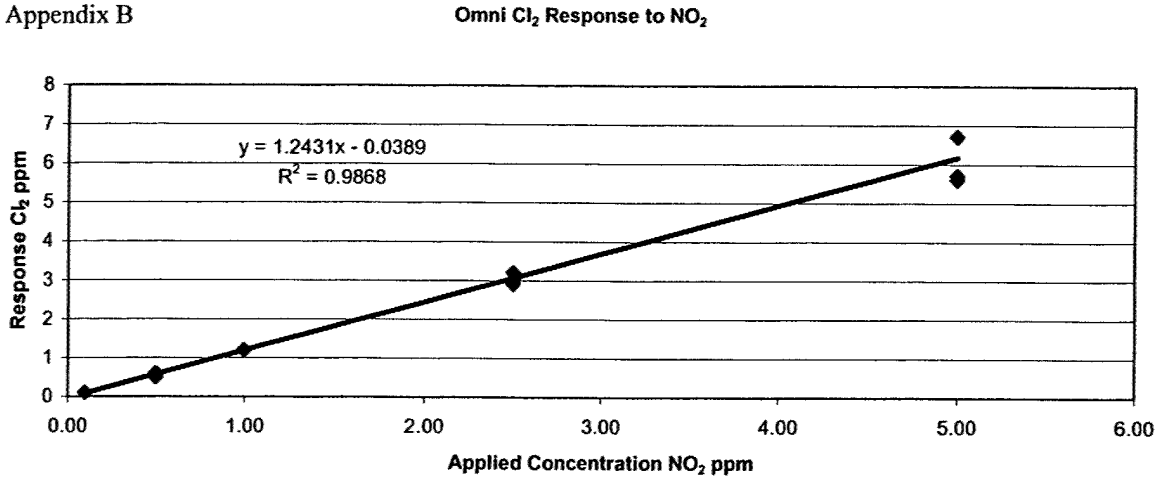


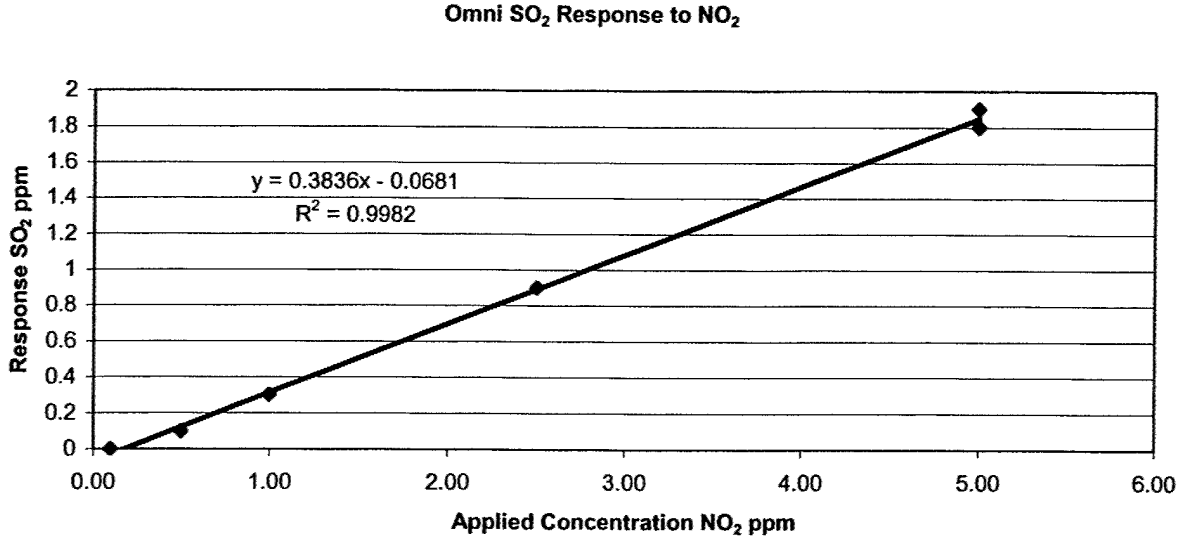
Omni SO_2

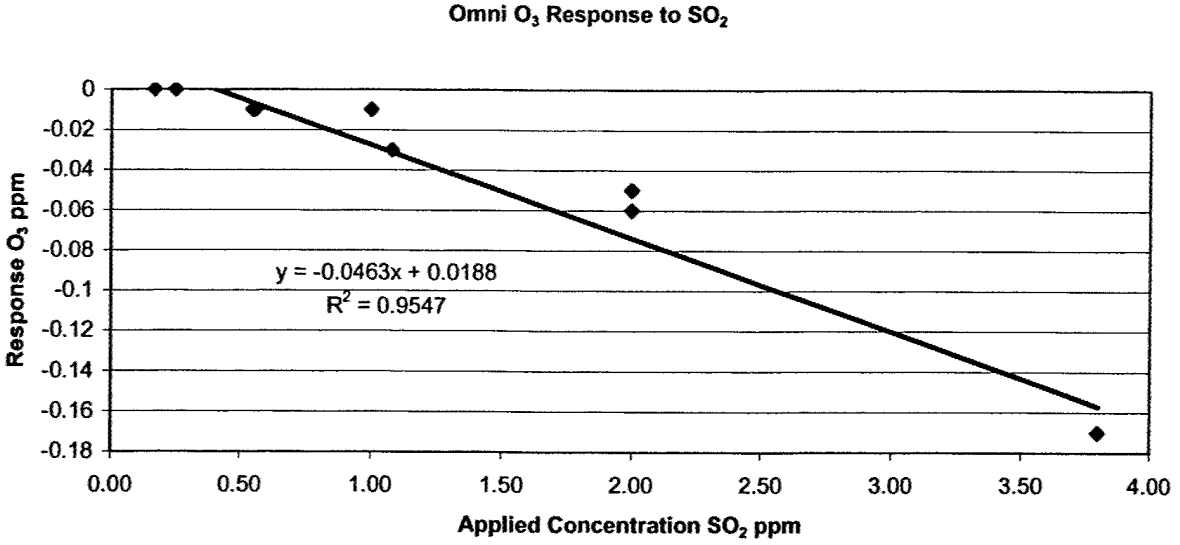



PhD5 SO_2
y = 0.6791x - 0.3724
R^2 = 0.9564
Response SO_2 ppm
Applied Concentration SO_2 ppm
0
2
4
6
8
10
12
14
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00

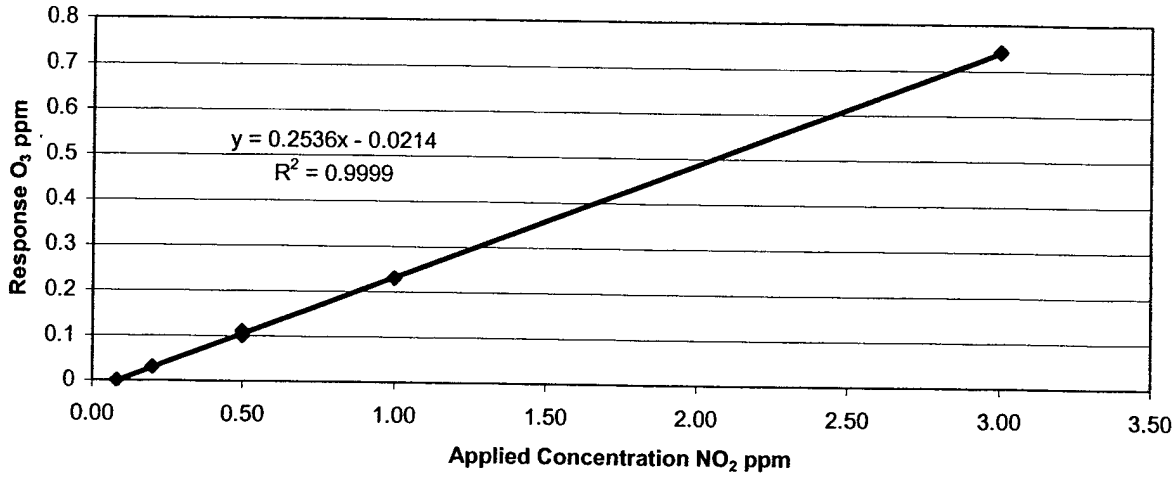
Appendix B


Omni Cl_2 Response to NO_2
y = 1.2431x - 0.0389
R^2 = 0.9868
Response Cl_2 ppm
Applied Concentration NO_2 ppm
0
1
2
3
4
5
6
7
8
0.00
1.00
2.00
3.00
4.00
5.00
6.00

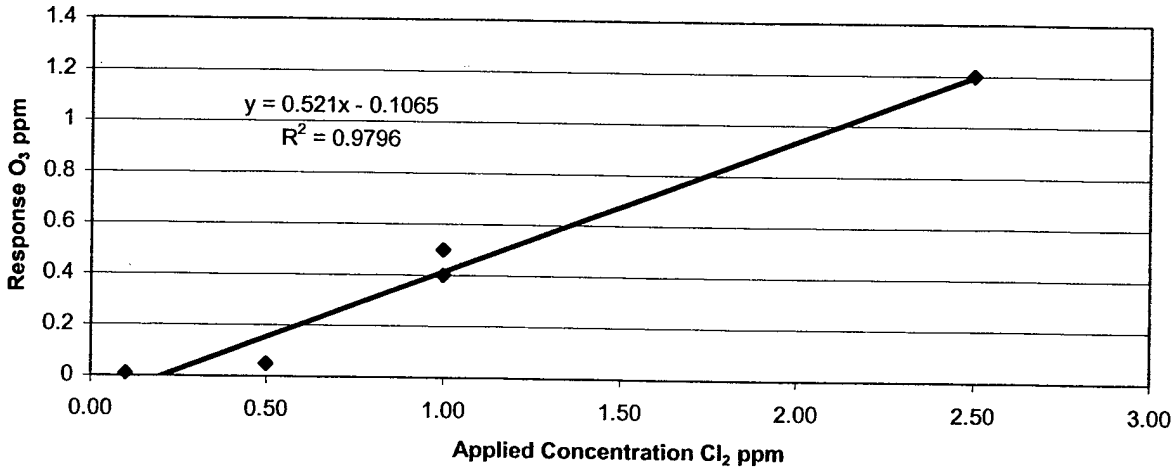

Omni SO_2 Response to NO_2
y = 0.3836x - 0.0681
R^2 = 0.9982
Response SO_2 ppm
Applied Concentration NO_2 ppm
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0.00
1.00
2.00
3.00
4.00
5.00
6.00


Omni O_3 Response to SO_2
y = -0.0463x + 0.0188
R^2 = 0.9547
Response O_3 ppm
Applied Concentration SO_2 ppm
0
-0.02
-0.04
-0.06
-0.08
-0.1
-0.12
-0.14
-0.16
-0.18
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00

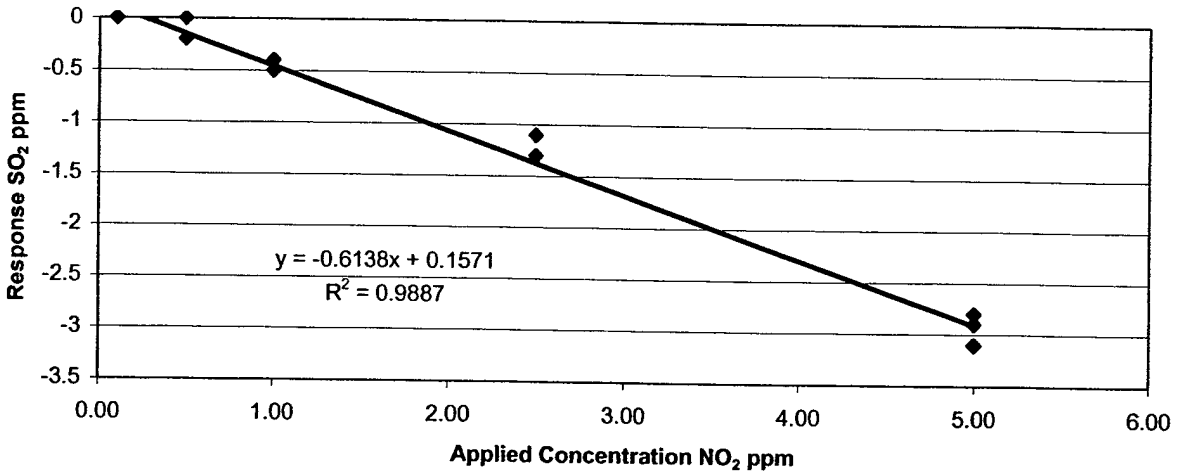
Omni O_3 Response to NO_2



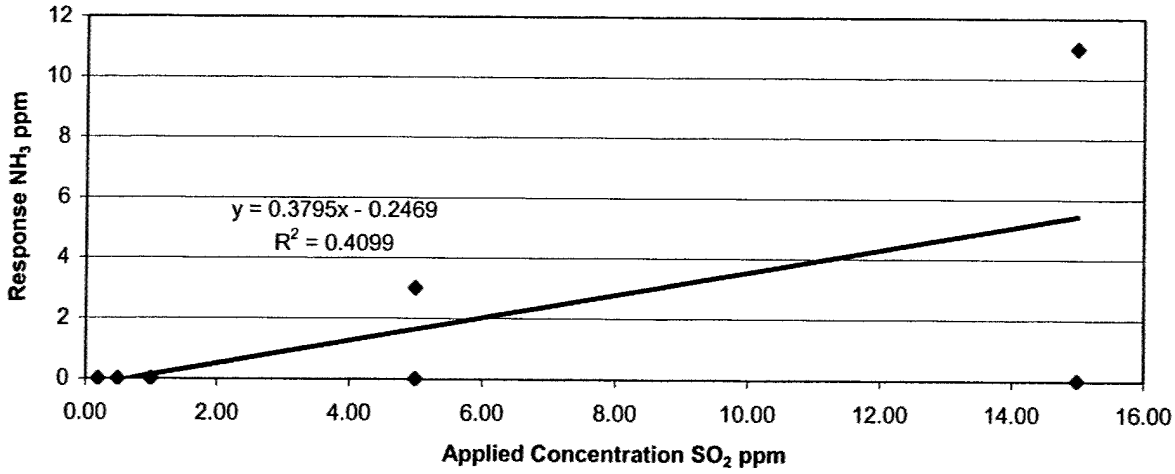
Omni O_3 Response to Cl_2



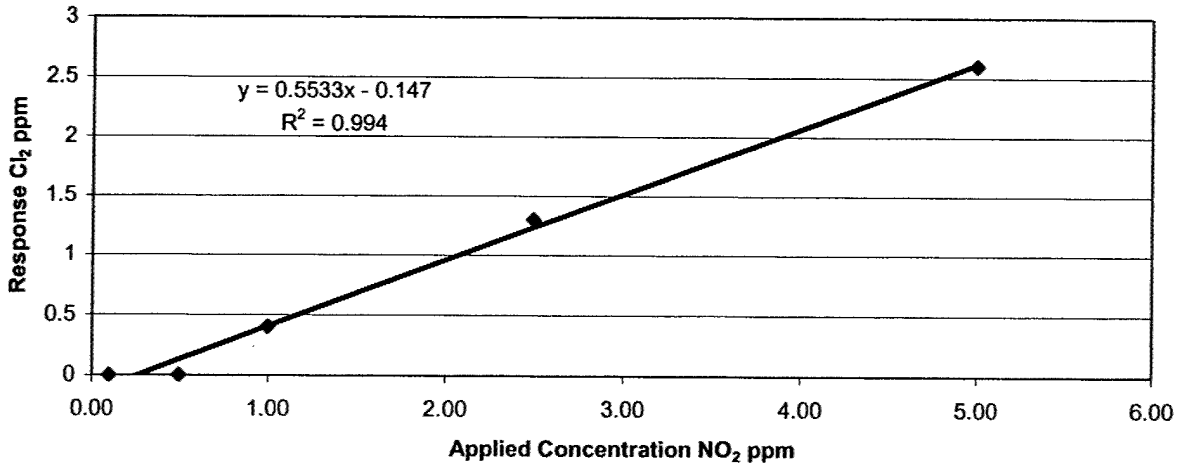
PhD5 SO_2 Response to NO_2



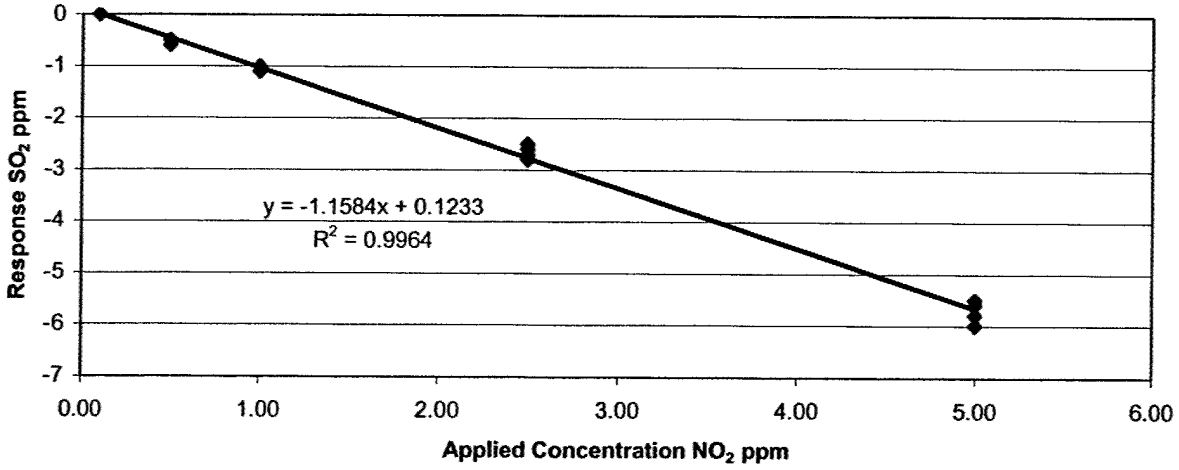
iTX NH_3 Response to SO_2



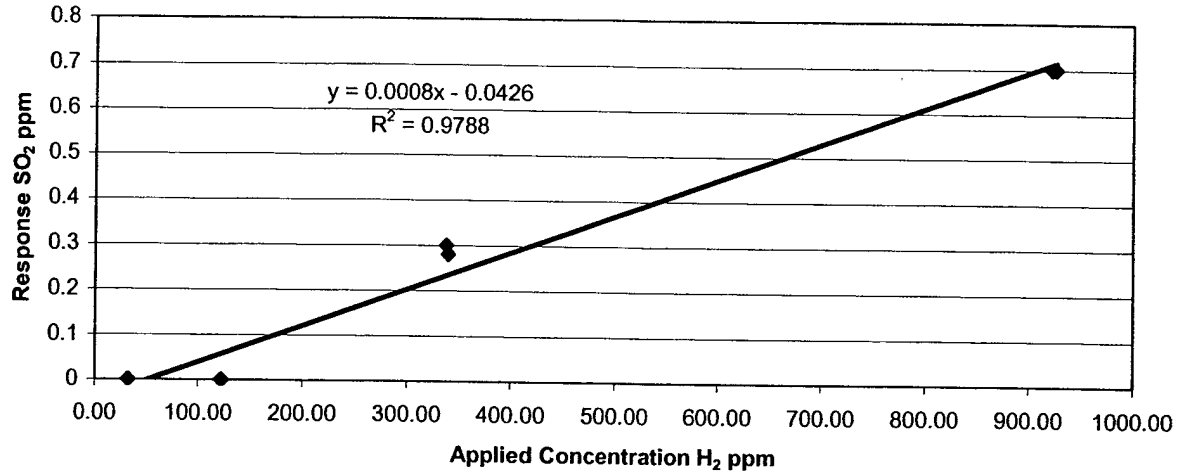
iTX Cl_2 Response to NO_2



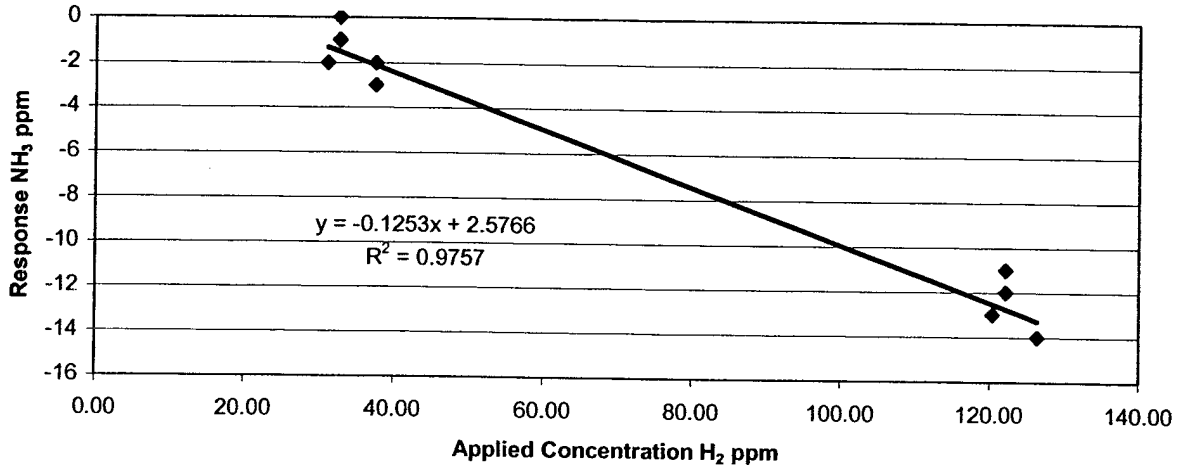
iTX SO_2 Response to NO_2



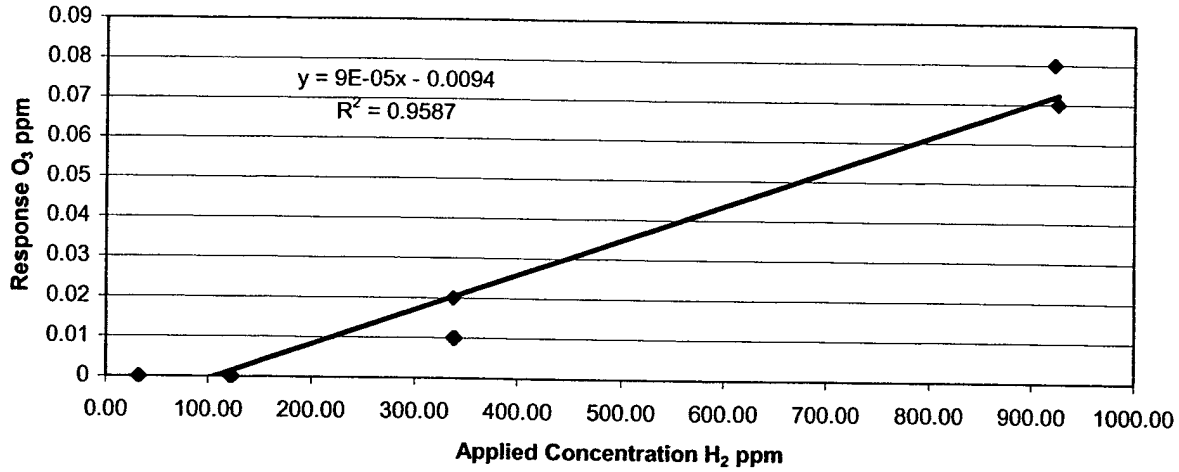
Dräger SO_2 Response to H_2

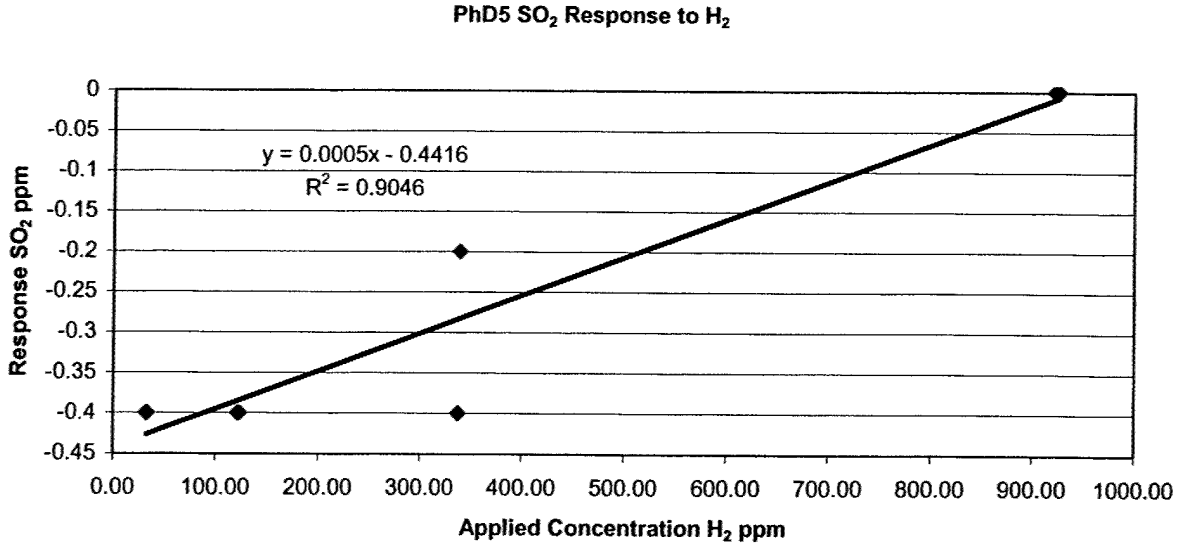


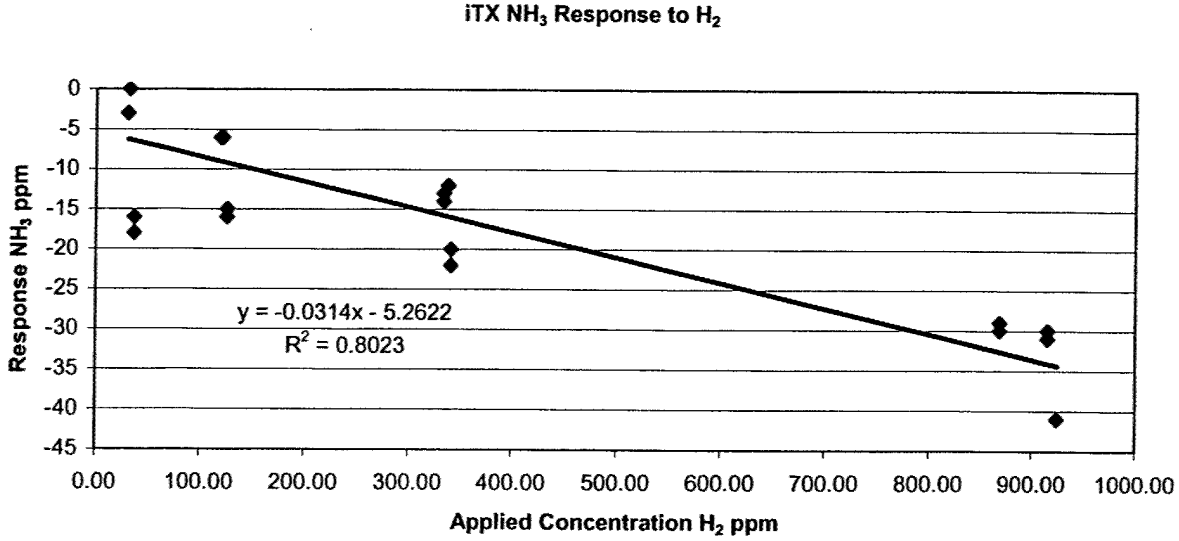
Omni NH_3 Response to H_2



Omni O_3 Response to H_2

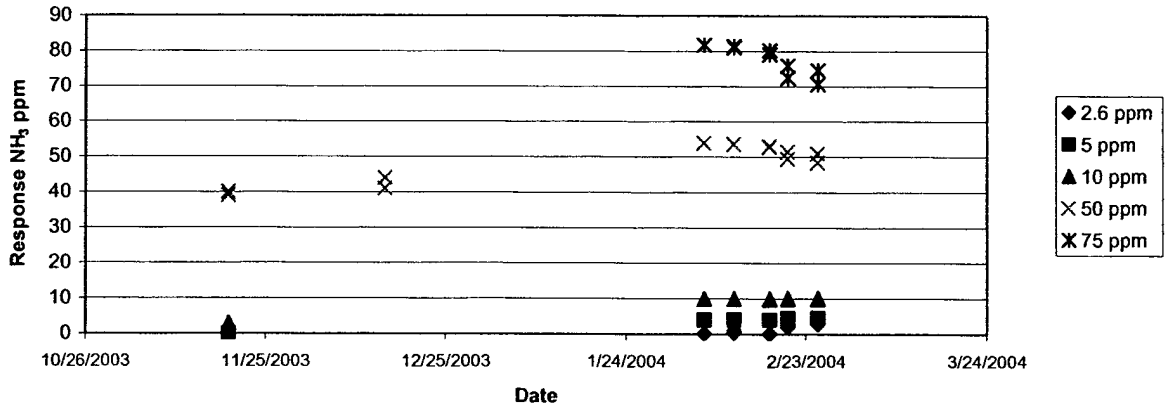



PhD5 SO_2 Response to H_2
y = 0.0005x - 0.4416
R^2 = 0.9046
Response SO_2 ppm
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
-0.4
-0.45
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
900.00
1000.00
Applied Concentration H_2 ppm

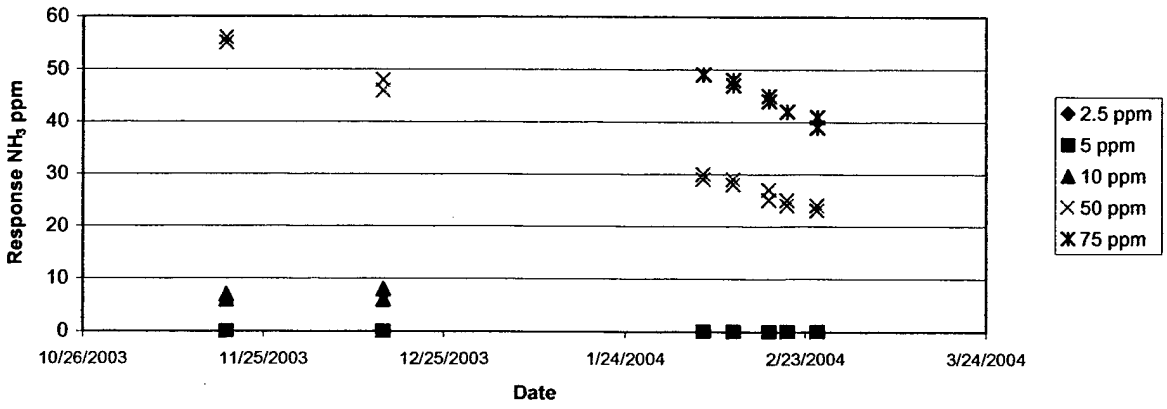

iTX NH_3 Response to H_2
y = -0.0314x - 5.2622
R^2 = 0.8023
Response NH_3 ppm
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
900.00
1000.00
Applied Concentration H_2 ppm

Appendix C

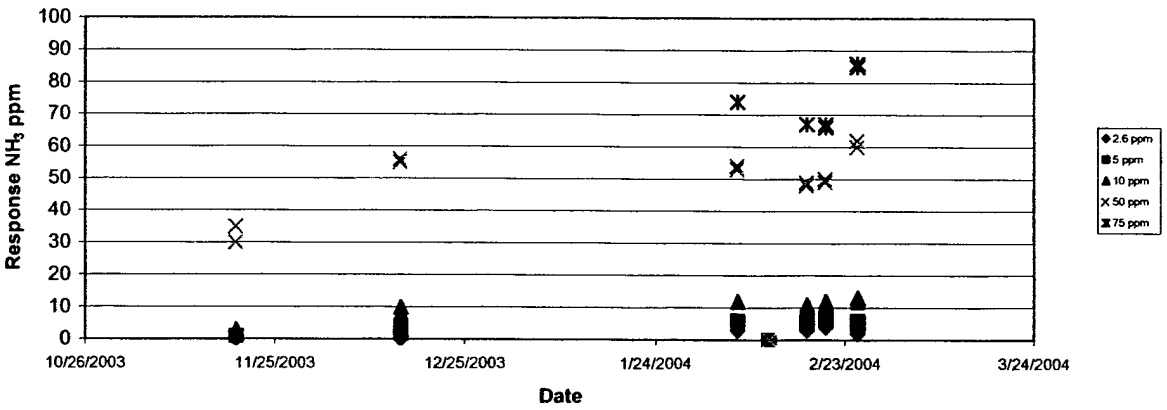
Dräger NH_3



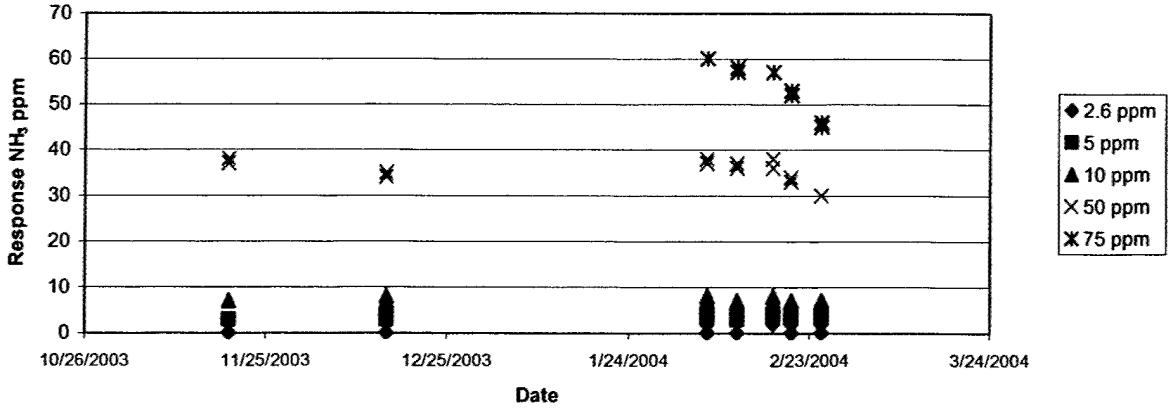
iTX NH_3



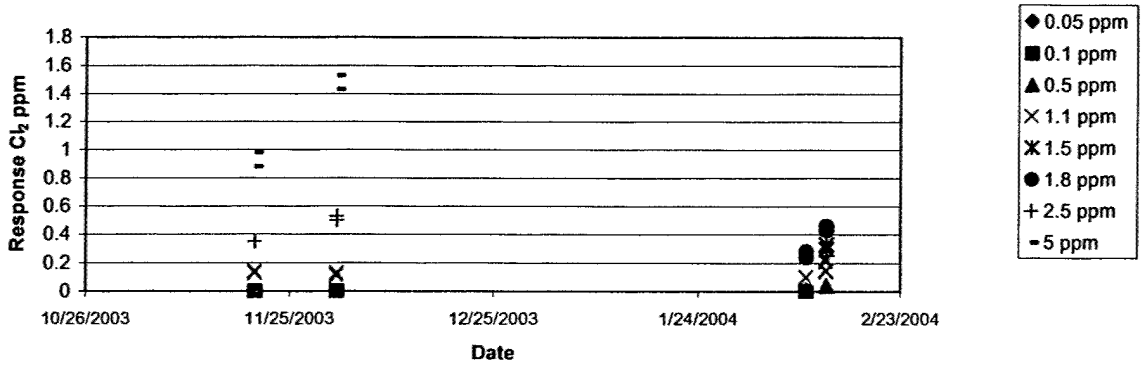
Omni NH_3



PhD5 NH_3



Dräger Cl_2



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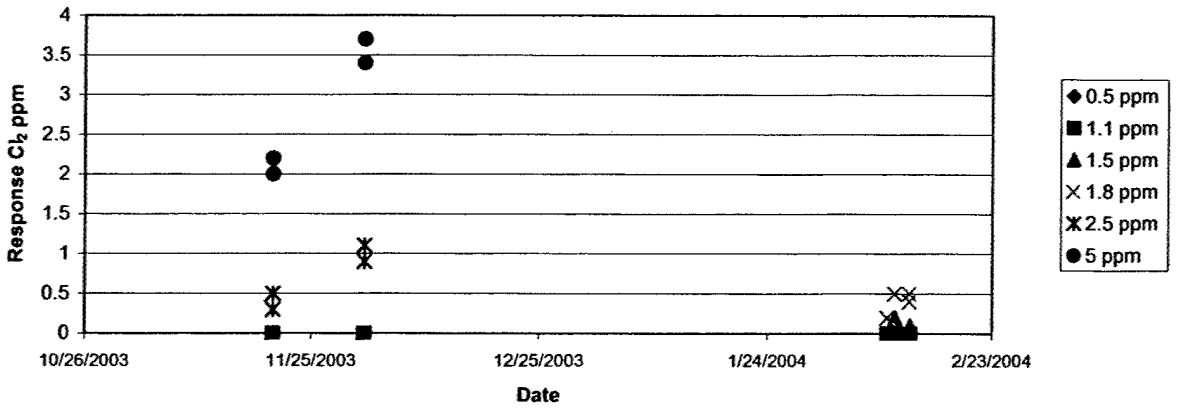

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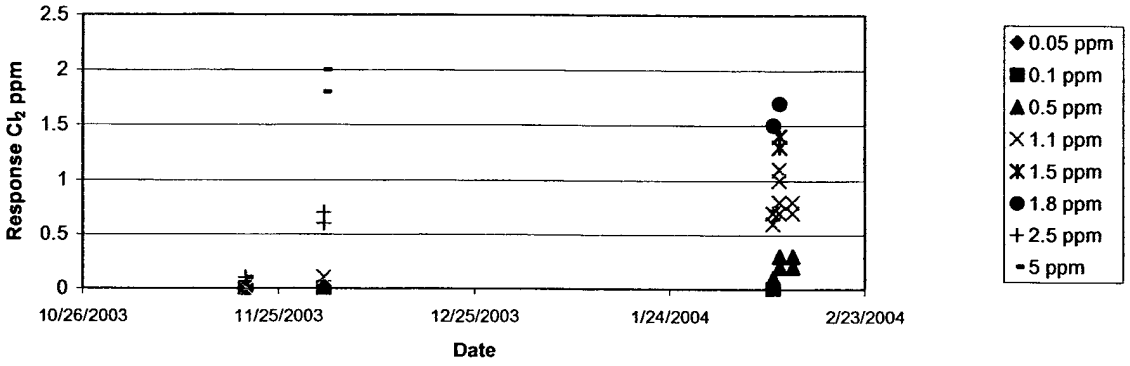

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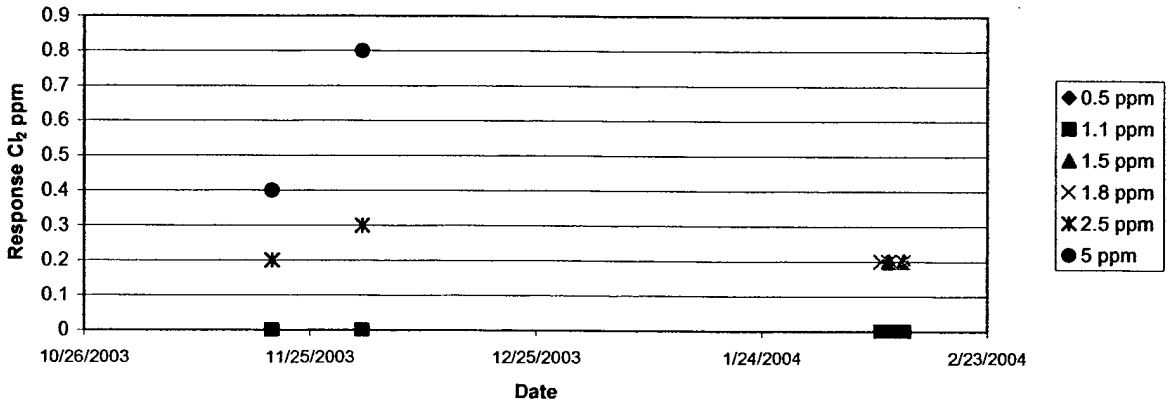

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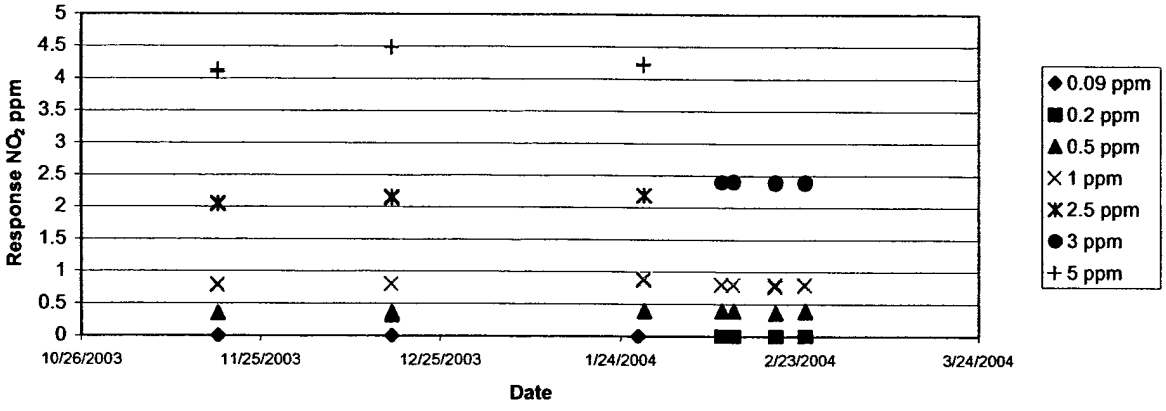

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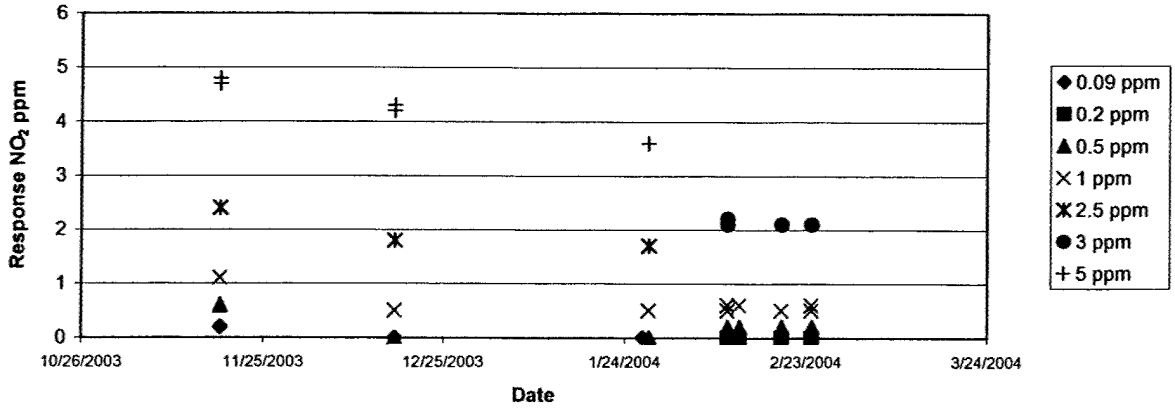

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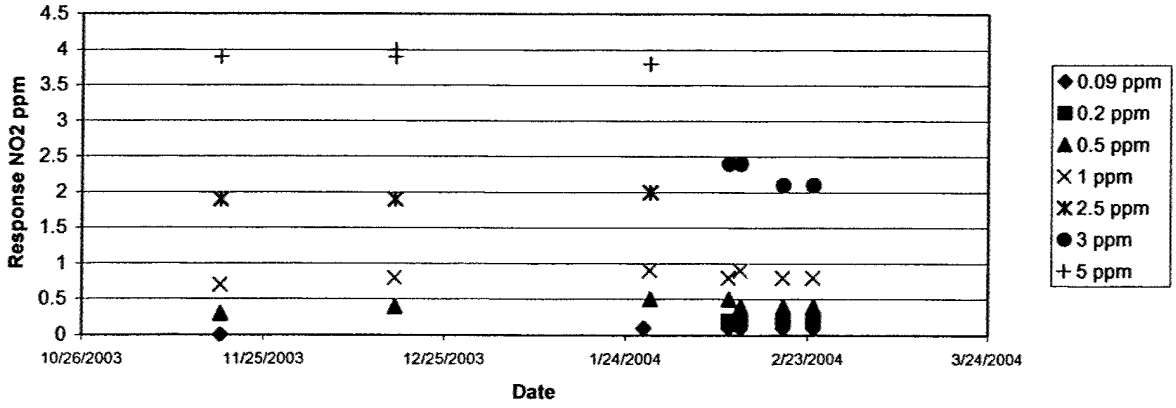

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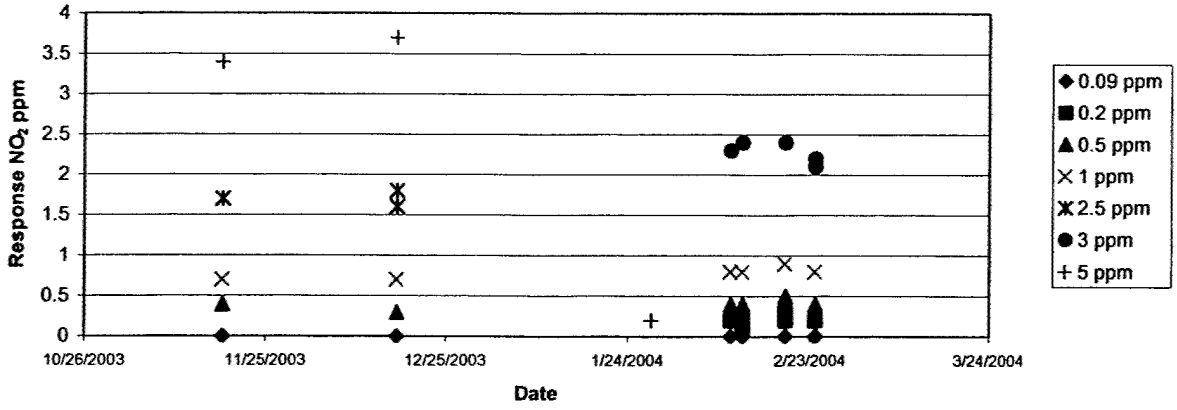
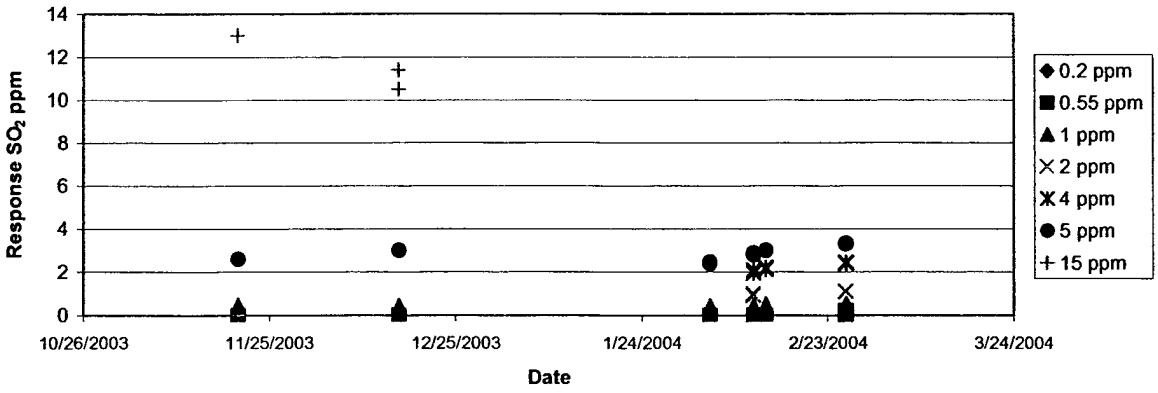


Dräger SO_2



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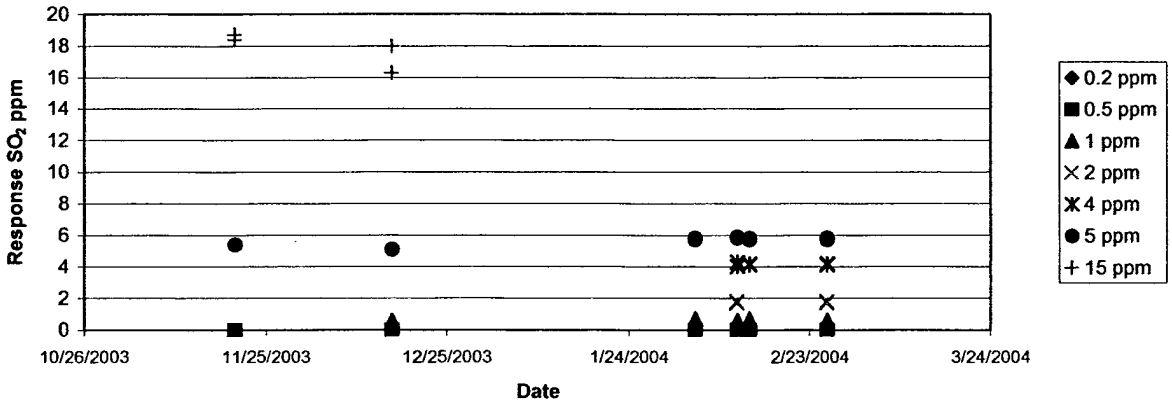

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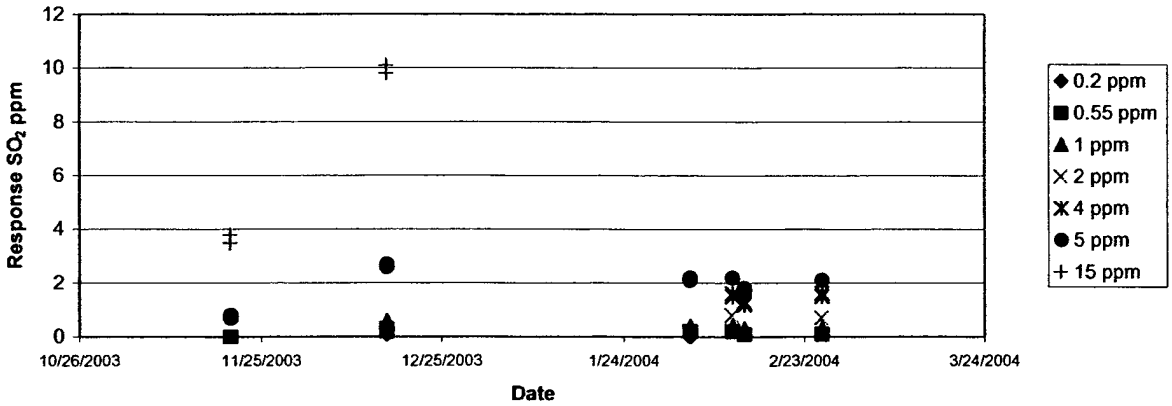

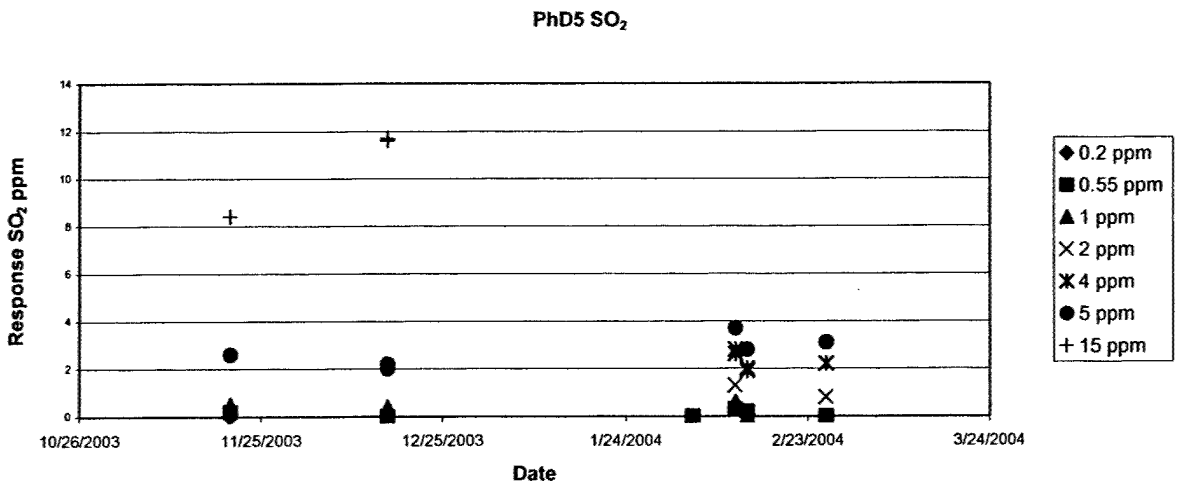
PhD5 SO_2
Response SO_2 ppm
14
12
10
8
6
4
2
0
10/26/2003
11/25/2003
12/25/2003
1/24/2004
2/23/2004
3/24/2004
Date
0.2 ppm
0.55 ppm
1 ppm
2 ppm
4 ppm
5 ppm
15 ppm